UNIVERSITY OF NAPLES FEDERICO II
Department of Chemical Sciences
XXVII° – PhD in Industry

"Air Pollution in the City of Naples: methods of measurements and prognostic models for the improvement of the air quality."

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Introduction.

The Air is a heterogeneous mixture consisting of gases and aerosols of various nature and size. Its composition changes according to space and time due to many chemical reactions and physical transformations. In the atmosphere the main part of the reactions occurs at environment temperature or, if high activation energy is needed, they are started photochemically,. These reactions are in the majority of cases represented by oxidation of gas due to the strongly oxidizing nature of the atmosphere.
In this scenario, the definition of atmospheric pollution is inevitably based on the effects that the concentration of various chemicals has on health, the human activities, the lives of other living beings and, in general, the ecosystem. According to **Dlgs. N°152/2006** the atmospheric pollution can be described as:

[…] every modification into the atmospheric air, due to the introduction of one or more substances which characteristics may adversely affect human health and the environment's quality […].

The possibility that the pollutants can be formed and transformed, leads to distinguish between *primary pollutants* emitted directly into the atmosphere, and *secondary pollutants* that originate by chemical or physical transformations in the air. The main primary pollutants are those emitted by combustion processes of any nature (e.g., unburned hydrocarbons in general), carbon monoxide, oxides of nitrogen (mainly in the form of monoxide) and Particulate Matter.
The atmosphere is therefore not in thermodynamic equilibrium, since the

pollutants are constantly active in many processes that influence the main components' concentrations. Following the emission into the atmosphere, primary pollutants are subject to diffusion processes, transport, deposition, and physical-chemical transformation processes that can lead to the formation of new species of pollutants.

The dispersion of pollutants in the atmosphere, caused by phenomena of turbulent diffusion and transport of air masses are closely dependent from the dynamic behavior of the lower layers of the atmosphere, as well as their removal, determined by deposition processes.

The consequence is that, for the study of the behavior of primary pollutants is necessary to know both the qualitative, quantitative and temporal emissions, as to have information on meteorological processes that regulate the dynamic behavior the lower troposphere (e.g., stability classes, wind direction and speed, etc..).

Among the processes of formation of secondary pollutants, particular importance is assumed by the series of reactions that occur between nitrogen oxides and hydrocarbons in the presence of sunlight. This chain of reactions leads the oxidation of nitrogen monoxide (NO) to nitrogen dioxide (NO_2), to production of ozone (O_3) and the oxidation of hydrocarbons, with the formation of peroxyacetyl nitrate (PAN), formaldehyde, nitric acid, sulphates and nitrates in the form particulate and transformation of organic compounds in organic particles (SOA).

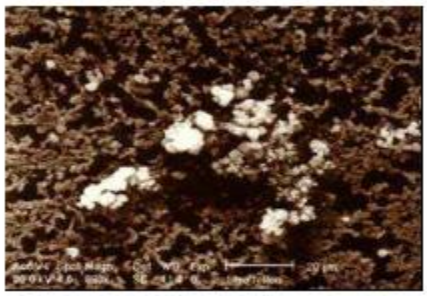
Of Course the atmospheric pollutants, both primary as secondary, have great mobility induced by convective and dispersive transport. The inhalable particulate behaves like a gas, while the upper diameter follows ballistic trajectories dominated by gravity force. All these components make the atmosphere a very complex reaction environment, difficult to

balance and susceptible to changes in the chemical nature and Weatherproof. To get an optimal framework of pollution in an urban area or in industrial areas is not enough to make measurements in the field. To have a prognostic approach aimed at real improvement in air quality, field measurements must be coupled with forecast predictions model, connected with another model for chemistry and transport of pollutants in the atmosphere. In this PhD work we carried out a campaign of monitoring of the main air pollutants (with particular attention to the chemical composition of particulate PM_{10}) by sampling and standard analysis credited at the European level. We developed a model for the meteorological area of the city of Naples using *WRF - The Weather Research & Forecasting Model (http://www.wrf-model.org/index.php)*. On the meteorological domain, we implemented a model of chemistry and transport of air pollutants through *CAMx – Comprehensive Air quality Model with eXtensions (http://www.camx.com/)*. At the end the project was carried out a theoretical comparison between experimental and theoretical data. The project is part of the XXVII Cycle Doctorate - *Doctorate in industry* - of the University of Naples Federico II in collaboration with the Majority of City of Naples and the Laboratory LAS – *Ambiente & Salute*.

Chapter 1.
The Particulate Matter[1]

Atmospheric particles originate from a variety of sources and have a range of morphological, chemical, physical, and thermodynamic properties. Examples of atmospheric particles include combustion-generated particles, such as diesel soot or fly ash; photochemically produced particles, such as those found in urban haze; salt particles formed from sea spray; and soil-like particles from re-suspended dust. Some particles are liquid; some are solid. Others may contain a solid core surrounded by liquid. Atmospheric particles contain inorganic ions, metallic compounds, elemental carbon, organic compounds, and crustal compounds. Some atmospheric particles are hygroscopic and contain particle-bound water. The organic fraction is especially complex, containing hundreds (probably thousands) of organic compounds. *Primary particles* are emitted directly from sources; whereas *secondary particles* are formed from gases through chemical reactions in the atmosphere involving atmospheric oxygen (O_2) and water vapor (H_2O); reactive species such as ozone (O_3); radicals such as the hydroxyl (COH) and nitrate (CNO_3) radicals; and pollutants such as sulfur dioxide (SO_2), nitrogen oxides (NO_X), and organic gases from natural and anthropogenic sources. The particle formation process includes nucleation of particles from low-vapor pressure gases emitted from sources or formed in the atmosphere by chemical reactions, condensation of low-vapor pressure gases on existing particles, and coagulation of particles. Thus, any given particle may contain PM from many sources. In fact, particles from a given source are composed as mixture of chemical components and, particles from different sources, may coagulate to form a new particle. In this way atmospheric particles may be considered as a mixture of mixtures. The

physical and chemical characteristics of particles are usually measured separately. Size distributions calculated by particle number it's used to calculate surface area. Volume distributions are often determined by physical means, such as electrical mobility, aerodynamic behavior, or light scattering. Chemical composition usually is determined by analysis of



collected samples, although some species can be measured *in situ*.

Fig.1.1: Particulate Matter on glass fiber filter

Fig1.2: Particulate Matter on TEFLON fiber filter

1.1 Particulate Matter: Definition

The Particulate Matter (PM) is a generic word used to individuate a large class of substances, chemically and physically different, presents in the environment air particles of different size. These type of particles can be generated in two different ways: as *primary particles* directly emitted from natural or anthropomorphic sources or as *secondary particles* generated in the atmosphere by transformation of oxides of sulfur (SO_X) and nitrogen (NO_X) and of volatile organic compounds (VOC).

The chemical and physics properties of Particulate Matter changes with a lot of different factors (e.g., time, meteorology, sources, region etc...). This intrinsec heterogeneous composition leaves particulate matter difficult to be classified and studied. Generally particulate matter si divided into two

classes depending on its diameter:

- **PM_{10}**: that is all the number of particles with a diameter less then 10 μm
- **$PM_{2,5}$**: that is all the number of particles with a diameter less then 2,5 μm
- **$PM_{1,0}$**: that is all the number of particles with a diameter less then 1,0 μm

Despite these three classes particles with these diameters tend to form themselves in different ways according to emission source, formation mechanism, composition and behaviour in the atmosphere.

1.2 Definition of Particulate Diameter

Generally the diameter of a spheric particle can be calculed by optic or electronic microscopy. However, the atmospheric particles are often not-spheric. For this reason to calcultate its diameters it's commonly used the *equivalent diameter* . Using this type of diameter we can consider the particles as spheres but with the same physic behaviour of atmospheric particles.

The *equivalent diameter* it's only one of the possible types of diameter used to study atmospheric particles. Other types of diameters are used in dependence of the processes of formation or in dependence of the particles sizes. For example for particles of small dimensions the most important process in the atmosphere is the diffusion. In these cases it's commonly used the *Stokes diameter.* For larger particles the gravitational parameters starts to be predominant and in these cases the *aerodynamic diameter* is used.

- **The Stokes Diameter (D_p)**

This diameter describes particles considering the drag that a particle has in a "fluid". In this way for a spheric particle the Stokes diameter coincides with the physic diameter while, for not-spheric particles the D_p coincides with the diameter of a sphere with the same drag of the particle. Generally Stokes diameter is used for particles distributions in diffusion processes. The D_p is independent from the density of the particle.

- **The Aerodynamic Diameter (D_a)**

it's defined as the diameter of a particle with speed equal to the gravitational speed and density $\rho = 1\ g/cm^3$. Particles as PM_{10} and $PM_{2,5}$ can be analyzed using the aerodynamic diameter. For particles with diameter less then 2,5 μm the diffusion process is the predominant one and is better to use the Stokes diameter.

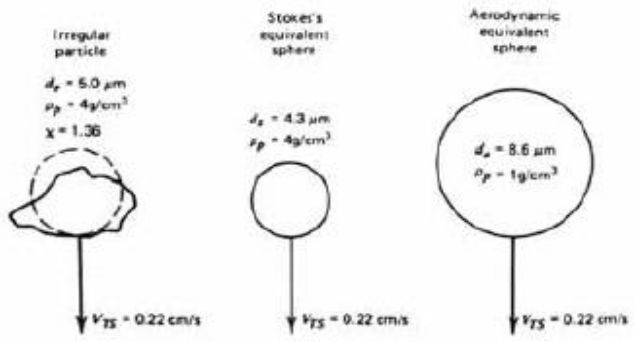


Fig. 1.3: Volume equivalent spherical diameter and aerodynamic diameter equivalent to irregular non-spherical particles

These two parameters are strictly related by:

$$D_a = D_p \left(\frac{\rho C_p}{C_a} \right)^{1/2}$$

(Eq.1.1)

Where ρ is the particle's density, C_p, and C_a are the Cunningham values calculated on D_p and D_a respectively. The Cunningham values are mathematical factors used to consider the not continues effects in the calculation of drag on small particles. The Cunningham values are functions between the particles diameter and λ that is the distance that one particle can cover straight on without any collisions with neighboring particles. These *C* factors assume great importance in the study of particles with diameter less then 1 μm, that means all that particles for which the mounting fluid can't be considered as continues. For large particles ($D_p > 5$ μm) C is assumed as 1. The equation 1 can be approximated to a simpler form considering two different cases about the free path λ. If λ is smaller then D_p :

$$D_a = D_p \, (\rho)^{1/2} \qquad (\text{for } D_p \gg \lambda)$$

(Eq.2.2)

It's possible to observe the direct proportionality between the aerodynamic diameter (D_a) and the density squared (ρ). This expression is generally used for particles with diameter ~ 0,5 μm.

On the other hand if D_p is smaller then λ:

$$D_a = (\rho) \, D_p \qquad (\text{for } D_p \ll \lambda)$$

(Eq.2.3)

The proportionality between D_a and ρ remains but without squared factor.

1.3 Particles Size Distribution

The particle size is a really important parameter in atmospheric analysis. From particle sizes, in fact, depend properties, effects and time of permanence in the atmosphere of particulate particles. Moreover the particles distribution influences their deposition into pulmonary system.

Elements like visibility, radiative equilibrium and climate are strongly influenced by light scattering across the particulate. Light scattering is strongly related to particle size distribution.

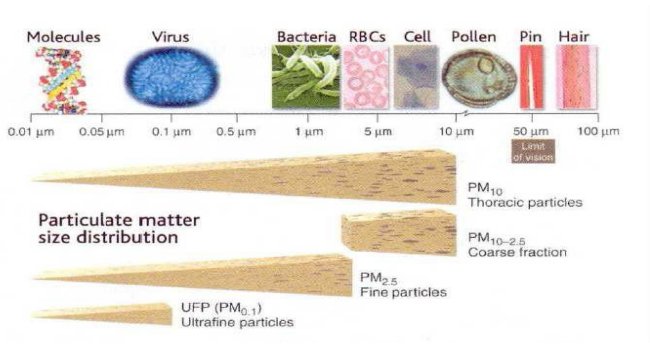


Fig 1.4: Particulate matter size distribution

The particles distribution of sizes is an important physical parameter governing particles behavior. Considering that atmospheric particles cover several orders of magnitude in particle size, size distributions are often expressed in terms of the logarithm of the particle diameter on the X-axis and the measured differential concentration on the Y-axis: $\Delta N/\Delta(\log D_p)$ = the number of particles per cm^3 of air having diameters in the size range from $\log D_p$ to $\log(D_p + \Delta D_p)$. Because logarithms do not have dimensions, it is necessary to think of the distribution as a function of $\log(D_p/D_{p0})$, where the reference diameter D_{p0} = 1 µm is not explicitly stated. If $\Delta N/\Delta(\log D_p)$ is plotted on a linear scale, the number of particles between D_p and $D_p + \Delta D_p$ is proportional to the area under the curve of $\Delta N/\Delta(\log D_p)$

versus logD_p. Similar considerations apply to distributions of surface, volume, and mass. When approximated by a function, the distributions are usually given as $dN/d(\log D_p)$ rather than $\Delta N/\Delta(\log D_p)$.

The fraction distribution of particulate matter is a topic widely studied. Essentially there are three conventional approaches for classification of particulate fractions:

- *"Modal"* based on the observation of different sizes and formation mechanisms.
- *"Dosimetric"* based on the different locations that the particles can be in the respiratory tract.
- *"Cut Point"* or a classification in line with the limits of the law and instrumental.

Considering the modal approach, Professor Kenneth T. Whitby, in 1971, observed that the particle size distribution was typically divided into three peaks which he called "modes". The entire distribution is characterized by a trimodal model consists of the sum of three logarithmic distributions.

In 1978 were published the results of analysis performed by Whitby on approximately 1000 samples of particulate air pollution. its analyzes were focused on the distribution of atmospheric diameter. In *Figure 1.5* he puts in relation the particle diameter $D_{p,}$ with the number of particles (c), the surfaces (b) and the volume (c). The graphs shown are in arithmetic scale for which the variables are relatable to the area under the curve in a quantitative way. From Whitby's data is possible to observe that, on average, particles are very small with diameters less than 0.1 μm. The average volume (and hence the mass) Highest is found in particles with a diameter> 0.1 μm.

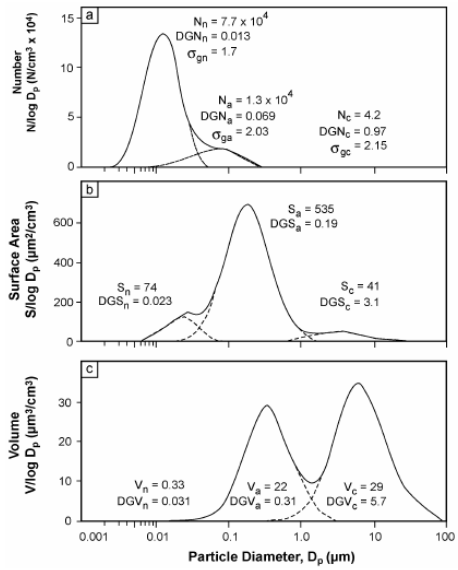


Fig. 1.5: Distribution of coarse (c), accumulation (a), and nuclei (n) mode particles bythree characteristics: (a) number, N; (b) surface area, S; and (c) volume, V for the grand average continental size distribution. DGV = geometric mean diameter by volume; DGS = geometric mean diameter by surface area; DGN = geometric mean diameter by number; Dp = particle diameter. [1]

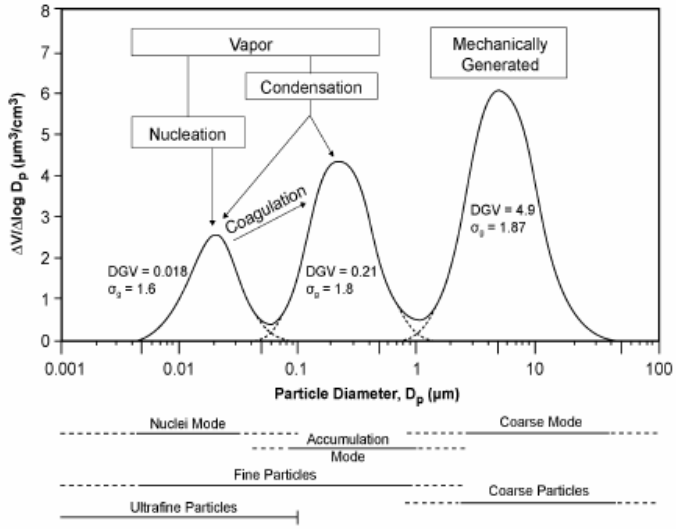


Fig.1.6: Volume size distribution, measured in traffic, showing fine and coarse particles and the nuclei and accumulation modes of fine particles. DGV (geometric mean diameter by volume, equivalent to volume median diameter) and Fg (geometric standard deviation) are shown for each mode. Also shown are transformation and growth mechanisms (e.g., nucleation, condensation,and coagulation).

The modes introduced by Whitby in 1978 showned in *figure 1.6* are the following:

1. *Nucleation Mode*: Freshly formed particles with diameters below about 10 nm, observed during active nucleation events. The lower limit, where particles and molecular clusters or large molecules overlap, is uncertain. Current techniques limit measurements to particles 3 nm or greater.
2. *Aitken Mode*: Larger particles with diameters between about 10 and 100 nm. The Aitken mode may result from growth of smaller particles or nucleation from higher concentrations of precursors.
3. *Accumulation Mode*: Particles with diameters from about 0.1 μm to just above the minimum in the mass or volume distributions which usually occurs between 1 and 3 μm.
4. *Fine Particles*: Fine particles include the nucleation, Aitken, and accumulation modes, i.e., particles from the lowest measurable size, currently about 3 nm, to just above the minimum in the mass or volume distribution which generally occurs between 1 and 3 μm.
5. *Coarse Mode* or *Coarse Particles*: Particles with diameters mostly greater than the minimum in the particle mass or volume distributions, which generally occurs between 1 and 3 μm.
6. *Ultrafine Particles*: Ultrafine particles are not a mode. In the air pollution literature, they are generally defined by size alone, i.e., particles with diameters of 0.1 μm (100 nm) or less. They include the nucleation mode and much of the Aitken mode. They may also be defined as particles whose properties differ from those of the bulk material because of their small size.

1.4 Sources and chemical Composition of Particulate Matter

Particulate air pollution has a variable composition. Usually, there are variable concentration of sulphates, nitrates, ammonium, organic carbon, heavy metals, marine salts, hydrogen ions and water. However, the concentration of these analytes can vary between the coarse fraction and the fine fraction of the particulate. On the other hand in addition to the primary compounds listed above we can find traces of elemental carbon, metals, and PAHs. The reason for this variability of the concentrations and composition must be sought in the great "reaction environment" that is the atmosphere and in particular the troposphere. To understand the atmospheric particulate matter and try to study it, it's necessary to understand that particulate matter has its formation in the atmosphere but also a change of its chemical composition in the period of time it spends in the air.

There are, in fact, two types of emissive sources from which it's possible to form particulate particles: natural emissive sources and anthropogenic sources.

- *Natural Emissive sources*: The chemical and mineralogical composition of atmospheric particles from the soil varies in relation to the geological characteristics of the geographic area in question. In general the average composition is given by: silicates (quartz clays, Cadinite, Illite, feldspar), carbonates (calcite, dolomite, calcium sulfates and iron oxides). However it is necessary to contextualize geologically the particulate sample to give an average chemical composition. Compounds of volcanic origin may be included in the particulate but usually their contribution is limited temporally and spatially. Sea spray contributes regarding the

fraction of sodium chloride (NaCl), magnesium chloride ($MgCl_2$) and various sulphates (mainly Na_2SO_4, $MgSO_4$, K_2SO_4). Sulfates, nitrates and organic aerosols are the main components of particulate air pollution from natural sources. Sulfates are obtained by oxidation of sulfur gases (SO_2) emitted by volcanoes or methyl sulfate ($(CH_3)_2S$) coming from the sea. The nitrates instead are obtained as end products of the oxidation of nitrogen oxides (NO_x) which are primarily derived from the soil and from solar radiation.

- *Anthropogenic Emissive Sources*: The main sources of air pollution are anthropogenic and located in large cities and industrial areas. In industrial coal the combustion is considerable as the primary source of particulate emission. The refineries, instead, contribute to the particulate matter emission in relation to the specific production of the factory itself. Metals such as nichel, vanandium, manganese and copper are generally issued. The anthropogenic secondary particulate mainly consists of nitrates sulfates and carbon. Nitrogen oxides are mainly from traffic and industrial processes. The oxidation leads to the formation of NO_X of nitric acid which can be neutralized and converted into ammonium ion NH_4^+ and nitrate. The biomass and fuel combustion are a major source of organic vapors. The aromatic compounds and non-methane hydrocarbons represent precursors of secondary organic vapor.

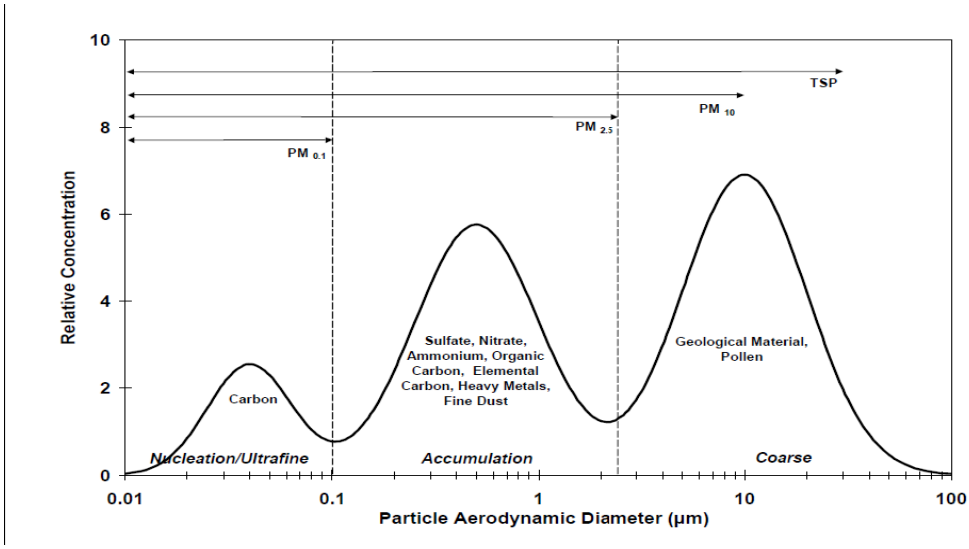


Fig. 1.7: Particle size distribution in the particulate mass indicating the main chemical components for each fashion.

1.5 Atmospheric Pollution: Effect on human health[2]

Several epidemiological studies have linked both PM_{10} as, specially, $PM_{2.5}$ with significant health problems, including: premature mortality, chronic respiratory disease, respiratory emergency room visits and hospital admissions, aggravated asthma, acute respiratory symptoms, and decreased lung function. Like the other criteria pollutants, the elderly, whose physiological reserves decline with age and who have higher prevalence of cardio-respiratory conditions, and children, whose respiratory systems are still developing and who spend more time outdoors, are most at risk from exposure to particulate matter. Also, individuals with preexisting heart or lung disease and asthmatics are sensitive to PM effects. Fine particulate pollution ($PM_{2.5}$), is of specific concern because it contains a high proportion of various toxic metals and acids, and aerodynamically it can penetrate deeper into the respiratory tract. Historically, the association between PM_{10} and mortality has been manifested in many air pollution

episodes such as those which occurred in Belgium (1930), Pennsylvania (1948), London (1952), New York (1953), and London (1962), where the number of deaths attributed to air pollution was 63, 20, 4000, 200 and 700, respectively. Several studies have demonstrated the relationship between low concentrations of PM_{10} and $PM_{2.5}$ and increase in daily mortality. A study conducted by *Pope, et al.,1996,* demonstrated the association between PM_{10} air pollution and cardiopulmonary and lung cancer mortality. The relationship was stronger for $PM_{2.5}$ than PM_{10}. $PM_{2.5}$ was associated with a 36% increase in death from lung cancer and 26% in cardiopulmonary deaths, the risk being higher for people over the age of 65. PM_{10} was not associated with lung cancer death.

The capacity of particulate matter to produce adverse health effects in humans depends on its deposition in the respiratory tract. Particle size, shape, and density affect deposition rates. The most important characteristics influencing the deposition of particles in the respiratory system are size and aerodynamic properties. The aerodynamic diameter of a particle is the diameter of a unit density

sphere having the same settling velocity as the particle in question, whatever its size, shape or density. Particles between 2.5 and 10 μm in aerodynamic diameter correspond to the inhalable particles capable to be deposited, in the upper respiratory tract. Particles with aerodynamic diameter smaller than 2.5 μm ($PM_{2.5}$), called fine particles, correspond to the respirable particle fraction capable of penetrating the alveolar region of the lung. Inhaled particles come in contact with surface of the respiratory system. These particles pass the proximal airway (throat and larynx) of the respiratory tract, and deposit in the tracheobronchial conductive airway of the lungs (bronchial and bronchiolar airway) or in the gas exchange region

(respiratory bronchioles, alveolar ducts, and alveoli of the lung parenchyma).

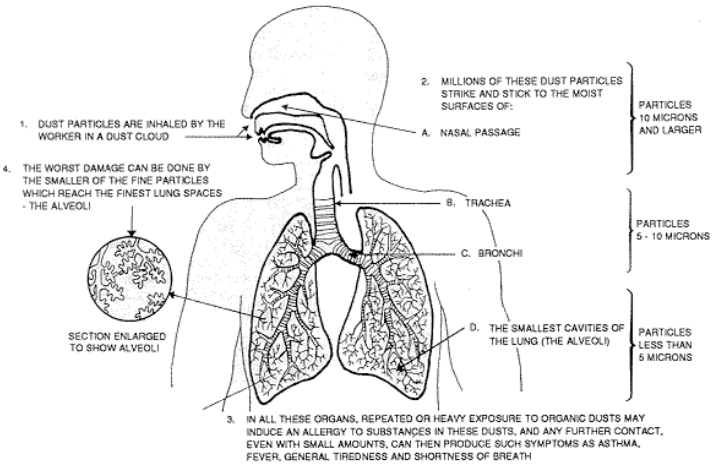


Fig.1.8: Depth of penetration of the particulate in the respiratory system as a function of particle size.

The health effects are also consistently observed in relation to the pollutants concentration and the exposure of urban populations in different parts of the world, both in developed countries and in developing countries. At the same time, the results of multiple clinical and toxicological studies have provided important information on the possible mechanisms of action by which pollutants shall perform the effects on human health, strengthening the biological plausibility of the observed associations in epidemiology. The increasing availability and wealth of information on the levels of environmental contaminants on estimates of human exposure, health information and the exposure-response relationships for the associations of interest, now allows to quantify the health impacts of considerable size.

The World Health Organization in 2006 showed that the reduction in atmospheric levels of PM10 annual average of 70 to 20 g/m^3 (or $PM_{2.5}$ from 35 to 10 g/m^3) would reduce by 15% the number of deaths due to air

pollution.

The PM_{10} and $PM_{2.5}$, among the pollutants, (the others are carbon monoxide, nitrogen dioxide and ozone) are mostly used synthetic indicators to estimate the health impact of air pollution and are strongly correlated with many other gaseous compounds frequently associated with a long series of health outcomes, ranging from acute respiratory symptoms to mortality for chronic effects.

These associations are due to the specific chemical composition of the particulate, which can contain both organic substances both inorganic such as polycyclic aromatic hydrocarbons (PAHs) and metals, whose chemical-physical properties, toxicological, and in some cases carcinogenic, make them particularly dangerous for health. The system, attacked by particulate, is the respiratory system and the most important factor for the study of the effects of PM is the size of the particles as it depends on the ability to penetrate into the respiratory tract; in this sense, there are three fractions:

- **inhalable fraction:** includes all particles that can enter the nostrils and mouth;
- **chest fraction:** includes particles that can pass through the larynx and enter the lungs during inhalation, reaching the tracheobronchial region (including the trachea and the respiratory ciliated);
- **breathable fraction:** includes particles small enough to be able to reach the alveolar region, including the non-ciliated airway and alveolar sacs.

The PM_{10} and $PM_{2.5}$ are respectively equivalent to thoracic and breathable fractions. Particulate matter deposited in the upper respiratory tract (nasal cavity, pharynx and larynx), can generate various effects such as

inflammation, irritation and dryness of the nose and throat, much more serious effects if the particles have absorbed acidic substances such as sulfur dioxide , nitrogen oxides, etc.. (*Brunekreef B. et al, 2005*). In addition to the particular structure of the surface, the particles can also adsorb from chemical carcinogens, which once entered in the respiratory tract, prolonging residence times, accentuate the effects. The smaller particles penetrate into the respiratory system at various depths and can spend long periods of time before they are removed, for this are the most dangerous. These, in fact, they can reach the lungs resulting in a possible absorption in the blood resulting in intoxication or aggravate also chronic respiratory diseases such as asthma, bronchitis and emphysema.

1.6 Particulate Matter's effect on climate

The atmospheric particulate absorbs and/or reflects the radiation coming from the sun as a function of the size and chemical composition of the particles that compose it, and the wavelength of the radiation itself. It therefore has a direct influence on the energy balance of the Earth which is linked to the climate and the overall effect will depend on the relative amount of light energy reflected back to space (backscattering) than that absorbed. Furthermore, the PM particles may act indirectly in favor of a cooling of the planet as act as condensation nuclei for the clouds, increasing the probability formation. In fact, if on the one hand, they reflect sunlight (reflection more efficient than that of oceans and land) leading to a cooling of the surface of the Earth, on the other hand, they also may have a role in the absorption phenomena of infrared Earth radiation, contributing to global warming. Particulate matter also has effects on the urban microclimate: in fact, in urban areas air pollution contributes to the "*heat island*" effect,

created by the high overbuilding of the city, by inhibiting the loss of long-wave radiation at night. In addition to this, the particulate matter on large cities can reduce by more than 15% the amount of solar radiation reaching the ground, obvious effect especially when the sun is low on the horizon. The path traveled by the light through polluted air increases when the sun's height decrease. So, given amount of particulate matter, solar energy will be reduced in a more intense in cities at high latitudes and during the winter.

PM Summary	Fine Particle	Coarse Particle
Formed from	Gases	Large solid/droplets
Formed by	Chemical reaction; nucleation; condensation, coagulation; evaporation of fog and cloud droplets in which gases have dissolved and reacted	Mechanical disruption (e.g. crushing, grinding, abrasion of surfaces); evaporation of sprays; suspension of dusts
Composed of	Sulfate (SO_4^{2-}); Nitrate (NO_3^-); ammonium (NH_4^+); hydrogen ion (H^+); elemental carbon; organic compounds (e.g. PAHs, PNAs); metals (Pb, Cd, V, Ni, Cu, Zn, Mn, Fe); particle bound water	Resuspended dust (e.g. soil dust,vstreet dust); coal and oil fly ash; metal oxides of crustal elements (Si, Al, Ti, Fe); $CaCO_3$, NaCl, sea salt; pollen, mould spores; plant/animal fragments; tyrewear debris
Solubility	Largely soluble,deliquescent Hygroscopic and deliquescent	Largely insoluble and non-hygroscopic
Sources	Combustion of coal, oil, gasoline, diesel, wood; atmospheric transformation products of NO_X, SO_2 and organic compounds including biogenic species (e.g. terpenes); high temperature processes, smelters, steel mills, etc.	Resuspension of industrial dust and soil tracked onto roads; suspension from disturbed soil (e.g. farming, mining, unpaved roads); biological sources; construction and demolition; coal and oil combustion; ocean spray
Lifetimes	Days to weeks	Minutes to Hours
Travel distance	100s to 1000s of kilometers	<1 to 10s of kilometers

Tab.1.1: Summary of the main main features of atmospheric particulate divided in fine particles and coarse particles. The table shows variables as: emission sources, processes of formation, chemical content average duration in the air and distance in indoor air. [1]

Compared to the surrounding rural areas, the relative humidity of the city is

generally lower than 2-8%; this is due to the fact that the cities are hotter and that the storm water run off quickly, but nevertheless cities clouds and fog frequently form due to human activities in urban areas that produce large amounts of particles that act as condensation nuclei, facilitating the formation of mists, and, when the nuclei are numerous, hygroscopic water vapor condenses on them rapidly, sometimes even in situations of undersaturation, thus causing an increase in precipitation on cities due to the particulate air pollution.

1.7 The other atmospheric pollutants

1.7.1 Carbon Monoxide (CO)

Carbon monoxide is a component odorless, colorless, tasteless, gaseous temperatures above -192 ° C, which are not appreciably soluble in water and with weight equal to 96.5% of the weight of the air. The formation of carbon oxides can take place according to three processes [*Finzi, 2001*]:

- *Incomplete combustion of carbon or carbon-containing compounds.* The reactions involved are essentially the following:

$$2C + O_2 \longrightarrow 2CO$$

$$2CO + O_2 \longrightarrow 2CO_2 \qquad \textbf{(reac.1)}$$

- *high temperature reaction between CO_2 and carbon-containing compounds*:

$$CO_2 + CO \longrightarrow 2CO \qquad \textbf{(reac.2)}$$

- *dissociation at high temperatures of CO_2 into CO and O* (in high temperature combustions):

$$CO_2 \longleftrightarrow CO + O \qquad \textbf{(reac.3)}$$

Industrial emissions of CO are essentially due to the fixed combustion of coal, fuel oil, wood. Another type of CO emissions are those due to steel processes. They consist in the enrichment of minerals in sinter plants,

production of pig iron in the blast furnace and in the activity of the foundry. There are also emissions due to biological and geophysical processes such as volcanic activity, emissions of natural gas, electrical discharges during storms etc.

Overall emissions of CO and the long persistence in the air, would be enough to double every 4-5 years, the atmospheric concentration world, but given that this does not occur, it is hypothesized the ability of some microorganisms commonly found in soil removed very quickly the carbon monoxide present in the atmosphere. It seems, in fact, that this type of removal is predominant compared to adsorption by plants and oxidation of CO in the atmosphere in the presence of oxygen. Unfortunately, the CO is mainly produced engines of cars in urban areas, where the ground is paved and then unsuitable adsorption. So that the CO can harm plants must reach concentrations exceeding 100 ppm for long periods, but the current conditions of concentration are far from these levels.

At the end, for what concern the effect on men, it is known that inhalation of air to high concentration (greater than 100 ppm) may lead to death, but pollution does not reach such high concentrations, the concentrations maximum observed in the urban environment are around 3-4 mg/m^3.

1.7.2 Sulfur Oxides (SO_x)

The combustion of materials containing sulfur will produce particular types oxides of this element: sulfur dioxide (SO_2) and sulfur trioxide (SO_3).

The main features of these two compounds indicated with general term of SO_x are the absence of color, the pungent smell and the high reactivity of SO_3. *The simplified mechanism of the formation of* SO_x is represented by two equilibria:

$$S + O_2 \leftrightarrow SO_2$$

$$2SO_2 + O_2 \leftrightarrow 2SO_3 \quad \textbf{(reac.4)}$$

The equilibrium reaction is slow. In this way the equilibrium conditions are never reached, and the concentration of SO_3 remains low. Moreover SO_3 gas may be present in the air only if the concentration of water vapor is low. Otherwise the SO_3 tends to combine with water vapor leading to the formation of droplets of sulfuric acid, according to the following reaction:

$$SO_3 + H_2O \leftrightarrow H_2SO_4 \quad \textbf{(reac.5)}$$

This conversion is influenced by many factors including humidity, the intensity, duration and the spectral distribution of sunlight, the presence of larger or smaller amounts of catalyst materials, absorbent and alkaline. this is the reason why the light of day and low humidity are very important both for oxidative phenomena that for photochemical reactions involving SO_2, NO_2 and hydrocarbons (due to the catalytic effect of nitrogen oxides on the oxidation of SO_2). At night, however, in humid conditions, fog or rain, the SO_2 is absorbed by drops of alkaline water present in the atmosphere and reacts with it with the consequent formation, in an appreciable speed, of sulfates such as ammonium and calcium sulfate. The sulfur in the atmosphere comes to about two-thirds natural sources (typically the volcanoes) and for the remaining part by human activity. The major sources of pollution from SO_x are stationary combustion plants for the production of energy: combustion of coal and fuel oils; are also to be considered the combustion in industrial plants in general, between which foundries, oil refineries etc.

1.7.3 Nitrogen Oxides (NO_x)

In terms of air pollution and oxides of nitrogen of greatest interest and concern are the NO and NO_2 from the reaction between N_2 and O_2 to high temperature (over 1210 °C) to form nitrogen monoxide that, oxidizing in turn, form nitrogen dioxide according to the following reactions:

$$\mathbf{N_2 + O_2 \leftrightarrow 2NO}$$

$$\mathbf{2NO + 2O_2 \leftrightarrow 2NO_2} \qquad \textbf{(reac.5)}$$

The amount of NO produced depends by the combustion temperature, the time of permanence at certain temperature of the gases during combustion and the amount content of free oxygen in the flame. The NO_2 production, on the other hand, increase with decreasing temperature, and takes place during cooling. High amounts of NO is converted into NO_2 once present in the atmosphere, for the occurrence of a photolytic cycle, direct consequence of the Solar light and NO_2 interaction. The phases are:

1. NO_2 absorbs energy from the sun in the form of ultraviolet light;
2. The absorbed energy cleaves the NO_2 molecules into NO molecules and oxygen atoms O;
3. Atomic oxygen atoms react with atmospheric oxygen (O_2) to produce ozone (O_3), a secondary pollutant;
4. Ozone reacts with NO to give NO_2 and O_2: the cycle closes.

If there were no other external molecules, NO_2 would be converted into NO then converted back into NO_2 without changes in the concentrations of the two compounds. But, on the contrary, the hydrocarbons present in the atmosphere interfere in cycle allowing that NO should be converted into NO_2 more rapidly than the NO_2 into NO and O. The consequence of this phenomenon is the accumulation of NO_2 and ozone (O_3). The largest

source of NOx pollution are pubblic and private transports. In particular, diesel engines produce more nitrogen oxides than petrol engines. Very high are also the emissions due to combustion in fixed installations, especially thermal power plants. Also little industrial processes which provide relatively small emissions of NOx, should not be neglected, because affect the environment and are very concentrated and localized.

The average residence time of the nitrogen oxides in the atmosphere is about three

days for NO_2, and about four to NO; This demonstrates the presence of natural removal mechanisms that eliminate nitrogen oxides from the atmosphere transforming them into nitric acid (HNO_3), which precipitates in the form of nitrates or rain. The NO_2 appears to be about four times more toxic than NO, but both are potential dangers to human health.

1.8 Models for air pollution

An air quality model is a tool that allows to estimate air concentrations of pollutants in a certain area and a certain amount of time that can range from a few hours or at most days (*short-term*), or months or years (*long -term*). There are a lot of models, very different in complexity and application fields. The regulatory environments that require the use of models on the air quality are still rising, and among these some examples are:

- the preparation of Environmental Impact Studies of works (*Legislative Decree 152/2006*) with reference to the impact of' work presented for the assessment on atmospheric environment;
- zoning of the region for the evaluation and management of air quality (*Legislative Decree no. 351/99* and *MD 2 April 2002 No. 60*);

- preparation of plans and programs for the protection and improvement of air quality (*Legislative Decree no. 351/99* and *MD October 1, 2002 No. 261*) with reference to the evaluation of the effectiveness of measures to reduce emissions;
- Strategic Environmental Assessment (SEA) (*Legislative Decree 152/2006, European Directive 2001/42 / EC*) with regard to the evaluation of the plan or program impact on the atmosphere evaluation.
- monitoring the quality of 'air as supplement to the sperimental measures (*Lgs.D. 351/99* and *M.D. 2 April 2002 No. 60*);

Moreover, these models are often necessary to determine the concentrations of pollutants in a certain region where they can not be directly derived from experimental measurements. Although, these measures are an essential step for the evaluation of air quality, are rarely sufficient to ensure adequate and exhaustive description, because, in general, the surveys are distributed unevenly over the territory and represent an average of the values of a finite interval of time.

The complexity of a complete discussion of the processes from which depends on the PM concentration into the atmosphere derives from the origin of Particulate Matter. They are difficult to describe due to the complexity of the oxidation reactions that occur in the atmosphere and that transform gases such as SO_x, NO_x and VOC in chemical constituents characterized by NO_3^-, SO_4^{2-} and OC (Organic Carbon).

The average life of the particulates in the atmosphere is of the order of a few days in the absence of rainfall (in this case involved processes of wet deposition relatively efficient), considering that the smaller particles (PM_{10})

have speed sedimentation almost negligible (dry deposition processes).

Advanced calculation codes treat different processes, which include the formation

condensable species, the distribution between gas and particles of condensable species and the evolution of the particle size.

In general, the calculation model used for the analysis of air quality, are composed of separate modules which cover each a part of the physical or chemical phenomena to be modeled (advection, diffusion, deposition and reaction).

Among the different models that simulate the dispersion and transformation of polluting substances into the atmosphere, for the work done in this thesis, we used the numerical code advanced CAMx (Including Air Quality Model with eXtensions) [*Environ, 2004*], not so much used in Italy, but recently entered in the code list recommended by 'US EPA (*Environmental Protection Agency*). The computer code is a three-dimensional model CAMx Eulerian grid that implements simplified mechanisms of atmospheric chemistry, with particular attention to photochemical processes involved in the cycle of nitrogen oxides and ozone in the presence of volatile organic compounds, incorporating modules for the description of complex phenomena related to the formation and transformation of aerosols..

Chapter 2.

Technical regulatory and legislative framework

2.1 Legislative developments regarding the air quality

The Italian legislation on air quality has evolved into an organized way during last years, both to the difficulty in identifying clear levels of intervention in a complex system such as the atmosphere, as for the consistent production and the legislative absence, for a long time, of a general rule that regulate uniquely all the different phenomena of air pollution. Italian legislation is, however, accompanied, in recent decades, by the EU legislation that all member countries are bound to implement. This has led to uniform the references and limitations, and the standardization of methods of measurement, at a community level.

In the European legislative framework, the attention is focused on the estimated mass of PM_{10} (although the Environmental Protection Agency EPA has introduced in the US a normative reference also introducing the measure in mass of $PM_{2.5}$). Starting in the early 80's in Italy have been implemented directives of the European community setting the *limit values* of air quality and the *guide values* (more restrictive, aiming at long-term protection of the individual). The following table (*tab.2.1*) shows in chronological order the decrees concerning the limits concentration for the particulate air pollution until 2002. In this date, with the **D.M. 60 02-04-2002** Italian Governament introduce for the first time the $PM_{2.5}$ as a significant pollutant in atmosphere. With this Ministerial Decree A target value is set for air monitoring of $PM_{2.5}$. The limit value on a 24 hour

average is 50 + 25 μg/m^3(of tolerance). This value has to define and gradually reduce to 0% from 2005 until early 2010 and it not to be exceeded more than 7 times a year related to PM_{10}.

Decree	Limit Value	Guide Value
	Average on 24h [μg/m^3]	*Average on 24h [μg/m^3]*
D.P.C.M. 28-03-1983	300 (95% percentile in 1 year) 150 (period of 1 year)	-
D.P.R. 203 24-05-1988	-	100-150 FN[1] 40-60 FN[1] (on one year average)
D.M. 25-11-1994	300 (95% percentile in 1 year) 150 (period of 1 year)	60 (1996 - 1999) 40 (from 1999) referring to PM_{10}
D.M. 21/04/99 (introduces limitation in urban traffic)	300 (95% percentile in 1 year) 150 (period of 1 year)	60 (1996 - 1999) 40 (from 1999) referring to PM_{10}
D.M. 60 02-04-2002 (introduction of PM2.5)	50 + 25 (tolerance of 50%) by gradually reducing to 0% after the entry into force of the decree until the beginning of 2005, not to be exceeded more than 35 times a year related to PM_{10}	40 + 8 (tolerance of 20%) by gradually reducing to 0% after the entry into force of the decree until the beginning of 2005, referred to the PM_{10}
	50 + tolerance to define and gradually reduce to 0% from 2005 until **early 2010** not to be exceeded more than 7 times a year related to PM_{10}	20 + 10 to be reduced gradually to 0% from 2005 until **early 2010** related to PM_{10}

Tab.2.1: Chronological order of the enactments relating to particulate air pollution and air quality Excluding the actual Legislative Framework.. (1) The initials FN indicates that the concentrations should be measured by the method of blacks smoke. The calculation of the 95% percentile should be selected from the values actually measured. All values will be shown in a list in ascending order: $X_1= X_2= X_3=....= X_k= ....= X_{N-1}= X_{N.}$
The 95° percentile is the value of the element of k rank, for which k is calculated by the following formule: k = (q*N) where q is equal to 0.95 and N is the number of values actually measured. The value of k = (q * N) should be rounded to the nearest whole number.

2.2 Legislative Decree. 13th August 2010, n. 155

Italian legislation currently in force in relation to the "air quality" is governed by **Legislative Decree. August 13, 2010, n. 155** transposing the **European Directive 2008/50 / EC** on ambient air quality and cleaner air for Europe. This decree repealing the following decrees of our legislation:

Legislative Decree August 4, 1999 n. 351: *"Implementation of Directive 96/62 / EC on the assessment and management of air quality"* transposing the Directive 96/62 / EC, defining a new strategy for air quality control through the subsequent adoption of decrees derivatives that cancelled much of the previous rules. The decree identified the process of assessment of air quality in the region.

DM April 2, 2002 n. 60: *"Enforcement Directive 1999/30 / EC of 22 April 1999 relating to limit values for ambient air quality for sulfur dioxide, nitrogen dioxide, oxides of nitrogen, particulate matter and lead to Directive 2000 / 69 / EC on ambient air quality limit values for benzene and carbon monoxide"*. This decree transposed the directives set and progressively repealed by the 203/88 (to the extent that this was the limit values and guiding values for air quality) and its implementing decrees. The decree, in line with the Framework Directive, provided allowances as transients in relation to different limit values and the time limits to be achieved. Tolerances are not limits, but represent pollution levels according to a fixed limit value percentage, decreasing continuously year after year, until it reaches the limit value. This condition provided a guide for the speed needed for the levels of pollutants to be reduced and to achieve the limit values within the set deadlines. Exceeding the margin of tolerance in a zone or agglomeration was indicative of the need to implement a plan or

rehabilitation program.

The Legislative Decree 183 of 31 May 2004 transposing *Directive 2002/3 / EC* relating to ozone in the air and identified the alarm thresholds and information for concentrations of ozone in the air. As for the other pollutants were fixed criteria of information, both in normal conditions and in the states of alert, on the levels of concentration of 1 hour and 8-hour recorded.

The Legislative Decree n. 152 of August 3, 2007 transposing *Directive 2007/107 / EC* relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, identifying methods of sampling and analysis and setting the values and objectives thresholds evaluation for the above parameters.

The decree establishing a unified regulatory framework on assessment and management of ambient air quality in order to:

- identify objectives for ambient air quality designed to avoid, prevent or reduce harmful effects on human health and the environment as a whole;
- assessing the ambient air quality on the basis of common methods and criteria throughout the national territory;
- obtaining information on ambient air quality as a basis to identify measures to be taken to combat pollution and the harmful effects of pollution on health

  human and the environment and to monitor long-term trends;
- maintain ambient air quality where good and improve it in other cases;
- provide the public with information on ambient air quality;
- achieve better cooperation between EU Member States in the field

of air pollution.

In particular are set:

- the limit values for ambient air concentrations of sulfur dioxide, nitrogen dioxide, benzene, carbon monoxide, lead and PM_{10};
- critical levels for ambient concentrations of sulfur dioxide and nitrogen oxides;
- alarm thresholds for ambient air concentrations of sulfur dioxide and nitrogen dioxide;
- the limit value, the target value, the exposure concentration obligation and
- the national goal of reducing exposure to ambient air concentrations of $PM_{2.5}$;
- target values for ambient air concentrations of arsenic, cadmium, nickel and benzo (α) pyrene.

Basically, the new decree confirms the previous limits for particulate matter, sulfur oxides and nitrous, ozone, benzene, carbon monoxide and lead but finally introduces $PM_{2.5}$ as a pollutant to monitor and control the air quality assessment and protecting the health of citizens. E 'was introduced annual limit value of 25 μg/m³ to be achieved by January 1, 2015.

For the protection of human health has been introduced, in addition, the average exposure indicator (AEI), the mean concentration of three calendar years, a value that is fixed at 20 μg/m³ by 2015 and 18 μg/m³ by 2020 .

Pollutant	Monitoring Period	Limit Value
Sulfur Oxide (SO_2)	Hourly (not to be exceeded more than 24 times in a calendar year)	350 $\mu g/m^3$
	Daily (not to be exceeded more than 3 times in a calendar year)	125 $\mu g/m^3$
Nytrogen Oxide (NO_2)	Hourly (not to be exceeded more than 18 times in a calendar year)	200 $\mu g/m^3$
	Annual	40 $\mu g/m^3$
Benzene (C_6H_6)	Annual	5 $\mu g/m^3$
Carbon Oxide (CO)	Daily mean calculated on 8 hours	10 mg/m^3
PM_{10}	Daily (not to be exceeded more than 35 times in a calendar year)	50 $\mu g/m^3$
	Annual	40 $\mu g/m^3$
$PM_{2,5}$	Objective Annual Value to be achieved by 2015	25 $\mu g/m^3$
Lead (Pb)	Annual	0.5 $\mu g/m^3$

Tab.2.2: Limit Value and Monitoring period for the main atmospheric pollutants. These values are calculated on a mathemathical average.

In 2004 the European Parliament and the Council of the European Union issued a directive **(2004/107/CE)** about Arsenic, Cadmium, Mercury, Nickel and Polycyclic Aromatic Hydrocarbons (PAHs) in ambient air. This is a directive in which it is expressly required that these compounds are sought in the PM_{10} particle fraction (*tab.2.3*).

Pollutant	Objective Value ($\mu g/m^3$)
Arsenic	6
Cadmium	5
Nickel	20
Benzo[α] pyrene	1

Tab.2.3: Arsenic, Cadmium, Mercury, Nickel and polycyclic aromatica hydrocarbons (PAHs) expressed as Benzo[α] pyrene, objective limits as reported by European Directive 2004/107/CE **.**

Heavy metals are considered as trace contaminants. They are generally found in very low concentrations in the environment. Some metals are essential micronutrients for the living species and only become toxic when their concentrations exceed natural values. Other metals such as Pb, Cd, Ni, and have no role in the life processes, but rather, can cause irreversible damage if present in high concentrations in nature.

Heavy metals are released by both natural sources such as: soil or volcanic eruptions both from anthropogenic sources like: Industrial Plants**,** Processes of combustion of petroleum and coal, vehicular emissions.

The Limit Value for Lead concentration in air samples is regulated by **DM 60/2002** and is calculated to 0,5 $\mu g/m^3$. For what concern Arsenic,

Cadmium and Nichel analysis, the **European Directive 2004/107/EC** establishes the target values shown in *table 2.4*.

Pollutant	**Limit Value** ***DM 60/02***
Lead (Pb)	0,5 µg/m3
Pollutant	**Objective Value** ***Dir 2004/107/EC***
Arsenic (As)	6 (ng/m^3)
Cadmium (Cd)	5 (ng/m^3)
Nichel (Ni)	20 (ng/m^3)

Tab.2.4: Summary table of heavy metals and their limits values as reported in European Directive 2004/107/EC

On Particulate Matter PM_{10}, besides the presence of Lead, Cadmium, Arsenic and Nickel, Chromium and Vanadium should also be searched for, even if they are not incorporated in the European directive. For these metals, in fact, the *World Health Organization* (WHO) shows the reference values (Guidelines in *tab.2.5*) and typical ranges of concentrations in the air depending on the type of area.

Pollutant	**Guidelines (ng/m^3)**	**Urban Areas (ng/m^3)**	**Industrial Areas (ng/m^3)**	**Remote Areas (ng/m^3)**
Cadmium (Cd)	(!)	1 - 50	1 – 100	0,1 – 10
Cromium (Cr)	(!)	4 - 70	5 – 200	0 – 3
Nichel (Ni)	(!)	3 - 100	8 – 200	0,1 - 0,7
Vanadium (V)	$1^{(*)}$	7 - 200	10 - 70	0 – 3
Pollutant	**Guidelines (ng/m^3)**	**Urban Areas (ng/m^3)**		**Remote Areas (ng/m^3)**
Lead (Pb)	0,5-1(*)	0,5 - 3		0,1 - 0,3

Tab.2.5: the reference values (Guidelines) and typical ranges of concentrations in the air depending on the type of area for the presence of Lead, Cadmium, Arsenic and Nickel, Chromium and Vanadium.
(*) Mean on 24 hours (!) Carcinogenic or probable carcinogenic

The Polycyclic Aromatic Hydrocarbons are hydrocarbons with an high Molecular Weight. The PAH's Molecules consist in two or more benzene rings, linked together with two or more carbon atoms in common. They are dangerous because they are semi-volatile and so they are particularly mobile through environmental matrices. Anthropogenic sources of production of PAHs are commonly:

- Transformation of fossil fuels
- Iron and Aluminium production
- Waste incineration
- Thermoelectric energy production
- Vehicular Traffic
- Tobacco Smoke

PAHs with more than four benzene rings remain in the atmosphere as gaseous mixtures for a short amount of time. They tend to condense and be adsorbed by carbon particles suspended. Particulate air pollution due to its high surface has high adsorption capacity of PAHs. Atmospheric exposure to PAHs is never tied to a single compound but a complex mixture.

The DM 25.11.94 staring at a target value of **1 ng/m^3** of the average annual concentration of benzo [α] pyrene. This particular PAH was adopted as a marker of cancer risk also by the **European Directive 2004/107/EC**. It is also recommended monitoring of five other PAHs significant, in the atmosphere and generally considered to be potentially hazardous to your health.

Name	IARC Classification
Benzo[a]pyrene	2A
Benzo[a]anthracene	2A
Benzo[b]fluoranthene	2B
Benzo[k]fluoranthene	2A
diBenz[a,h]anthracene	2B
Indeno[1,2,3-cd]pyrene	2B

Fig.2.1. IARC – *International Agency for Research on Cancer* classification for PAHs 2A in for probable carcinogenic, 2B for possible carcinogenic.

In this PhD work, we worked in accordance with the **European Directive 2004/107 / EC**, and we have demonstrated the ability to analyze 19 metals by ICP-MS (including those prescribed by law) and 16 PAHs by HPLC (including those prescribed by law) simultaneously. Using as sampling technique the gravimetric method, which provides for the collection of appreciable amounts of particulate matter and consequently, the sampling has been performed at relatively high flows (> 15 l/min). The gravimetric index is influenced by the presence of particles with high grain size that greatly contributes to the definition of the mass particulate collected. The reference method for the sampling and measurement of PM10 is described in EN 12341: 1999 *"Air Quality - Field Test Procedure for demonstrate equivalence reference methods for sampling about PM10 particles ".*

2.3 The technical standard UNI EN 12341: 2001

UNI EN 12341: 2001 describes the reference method and procedure for

field trials to demonstrate the equivalence of measurement methods compared with the reference method for the determination of suspended particulate PM_{10}. The procedure described in the standard is a practical method that allows institutions or European industries to assess any levy systems in ambient condition. The measurement method reference should consist of a sampler with an inlet orifice for PM10 directly coupled to a filter and regulator Flow measurement in its chain, with the gravimetric determination of the mass of PM_{10} collected on the filter. Must be used one of the following devices:

- *system at low volume*: LVS-PM10 sampler device
- *system loud*: sampler unit HVS-PM 10
- *system very loud*: device-PM10 sampler WRAC

The standard also defines the design criteria for the equipment samplers reference. In particular with regard to the 'appliance sampler LVS-PM10 the particulate is aspirated through the opening circumferential placed between the housing and the circular plate placed on top of this. The suction opening must be protected from rain and snow by means of a cover. Within the sampling orifice, the air flow is accelerated through 8 nozzle impactors then be directed towards the impact surface. Later, the airflow passes through a ventilation tube that leads to the filter mount. The latter must be suitable for insertion of circular filters having a diameter

between 47mm and 50mm. The diameter of the free area for the passage of air sampled through the filter must be between 40mm and 41mm. the nozzles impactors and impact surface must be cleaned regularly.

Furthermore, the impact surface must be lubricated, preferably with a silicon lubricant vacuum. Cleaning and lubrication must be performed at least every 20 samples. Depending on the concentration of PM10, cleaning

and lubrication must be performed more frequently (for example, only every 5 withdrawals). In order to facilitate the operations of cleaning and lubrication, the orifice input must be designed in such a way as to remove the plate impact from the bay. The instrument sampling system must be able to withstand the weathering. For example, the inlet orifice and the filter holder can be made of anodized aluminum and stainless steel; the filter holder can also be made of plastic (polycarbonate). The overall performance of the devices samplers are:

- the system LVS-PM10 is operating at a constant flow rate of (2.3 ± 2%) m^3 / h.
- the system HVS-PM10 is operating at a constant flow rate of (68 ± 2%) m^3 / h.
- the system WRAC-PM10 is operating at a constant flow rate of (77.9 ± 2%) m^3 / h.

To operate the equipment samplers reference HVS-PM10 and WRAC-PM10 should be used compressors having a suction flow greater than 100 m^3/h, while for the system LVS-PM10 must be employed vacuum pump carbon blades having a higher flow rate of 3 m^3/h. Between the filter and the vacuum pump or the compressor must be installed a sensor flow so as to obtain a correct measurement of the air flow. you have to also carefully check that all the air ducts between the filter support, flow sensor and pump or compressor are absolutely watertight. The filters used in the reference system and in the one in question must be handled in a similar way. Filters must be employed having a separation efficiency> 99.5% (preferably quartz fiber filters).

The filters unused and previously sampled must be rebalanced to same conditions: they must be placed for 48 h on special perforated trays open

but protected against dust inside a weighing chamber with air conditioning and exposed to a temperature of (20 ± 1) ° C and a relative humidity of (50 ± 5)%. Filters for very dry or very wet conditioning can be extended by 24 h. The resolution of the balance used must be at least 10 g. The balance must be installed and used in the weighing chamber.

The test method in the field requires the selection of test sites, taking into account the integrity of the site-wide macro-environment (type of location) and scale micro-environmental (area immediately surrounding the measuring station). On a macro-environmental place of sampling must be chosen so such as to represent both situations commonly encountered, both situations extreme. On a micro-environment must be respected at least the following basic rules:

- the flow around the orifice unit input sampler must be in any way disturbed; Furthermore, there should be no obstacles (balconies, trees, vertical surfaces or walls, etc.) that might influence air flow in the vicinity of the equipment samplers;
- inlets must be located at a sufficient distance from each from the other so as to avoid mutual interference on sampling (for such a device should not be in the vicinity of the discharge of the pump of the other);
- all inlets should be the same height (between 1.5m and 8m) from the ground;
- inlets should be positioned away from local sources of particulate in order to prevent dust clouds can enter directly in the device (for example, you must avoid proximity to chimneys residential heating).

The equivalence of a sampler device with the reference tool depends on the

following aspects:

- comparability sampler unit in question: the uncertainty of results obtained with the apparatus samplers concerned (obtained from double measurements) is used as a measure suitable to assess the comparability. Obviously different specimens of the same type of device sampler should behave the same way during the procurement the same fraction of SPM (suspended articulated);
- comparability sampler unit under review with the appliance sampler reference: ideally the device sampler examination and reference should take the same village of SPM (ie PM10). Then the function of equivalence to the observed reference y = f (x), which describes the ratio of the measured concentrations with the appliance sampler concerned ye the reference x, should approach the ideal function y = x to the extent required by the objectives of quality of the user.

2.4 The technical standard UNI EN 15549:2005

Chemical analysis of particulate filters was carried out according to the procedure laid down by the UNI EN 15549. The standard specifies a measurement method for the determination of benzo [α] pyrene (BaP) in ambient air particle and describes the features and presentation criteria for the measurement method, when it is used as a reference method.

The measurement method chosen include: handling and preparation of filters, sampling of BaP as a fraction of PM_{10}, ultrasonic extraction of samples, analysis by HPLC (High Performance Liquid Chromatography) with fluorescence detection (FLD) and quantification. The method is

applicable for measurements of BaP in the concentration range comprised, approximately, between 0,04 ng/m^3 and 20 ng/m^3.

2.5 The technical standard UNI EN 14902:2005

The European Standard specifes a method for determination of particulate lead (Pb), cadmium (Cd), arsenic (As), and nichel (Ni) in ambient air.

The method is divided into two main parts: first the sampling in the field and second the analysis in the laboratory. During sampling , particles containing Pb, Cd,As and Ni are collected by drawing a measured volume of ai through a filter mounted on a sampler designed to collect PM10 fraction of particulate matter. The sample filter is transported to the laboratory and Pb, Cd, Ni, and As are taken into a solution by closed vessel microwave digestion using nitric acid and hydroxygen peroxide. The resultant solution in analyzed by ICP -MS. This European Standard is applicable for measurements of Pb, Cd, As, and Ni as part of PM_{10} aerosol fraction in the concentration ranges listed in *table 7*:

	From	To
Pb	1 ng/m^3	4000 ng/m^3
Cd	0,1 ng/m^3	50 ng/m^3
As	0,5 ng/m^3	350 ng/m^3
Ni	2 ng/m^3	100 ng/m^3

Tab.2.6: concentration range for lead, cadmium, arsenic and nichel in ambient air and expecially in the particulate fraction according to UNI EN 14902:2005 standard method.

Chapter 3.
Air Quality Monitoring Campaign "*Napoli Est*".

3.1 The City of Naples and the district of *San Giovanni a Teduccio*

Naples is an Italian town of 957,954 inhabitants, capital of the homonym province and of the region Campania. It's located almost in the middle of the Gulf of Naples, between Vesuvius and the volcanic area of *Campi Flegrei*. Like all major Italian cities, has experienced the '60s an exponential economic and demographic growth, which has completely changed and changed his appearance. Like all big cities, soon found itself to face, and makes them still, with the problems of traffic and industrialization, with its negative effects such as air pollution.

San Giovanni in Teduccio is one of the neighborhoods of Naples, originally intended only for industrial systems, among still available territories between *Arenaccia*, the old *Ponte della Maddalena* and *Granilli* completely destroyed by bombing in 1943. The territory, although not very large (2.35 km2), has about 25,000 inhabitants and is one of the poorest suburbs of Naples, where the high population density, is not an adequate network of social services. The populous district is located between the State of Vesuvian towns, the highway Napoli-Salerno and is crushed by the harbor. Much of the area, a time, she was depressed and marshy, until, in the middle of the '400 land reclamation work began that led to the creation of the Royal Canal and a network of smaller channels. The site, currently, is instead characterized by the presence of brown fields and other assets, of port equipment and populous districts. Its industrialization, which began at

the end of '700, has been growing, reaching its peak in the period of the 50s and 70s, with the birth of thermal power plants, petrochemical, mechanical, textile, food, tanning and glassmaking. Some industries of that period are: *Stella* Factory for the production of tannin, the silk factory *Beaux*, foundries *Guppy* of 1852, the *Macry-Henry-Zino & C.*, 1839, mechanical workshops *Pattison* fate in 1864 and *Deluy-Granier* was born in 1872 and sold ten years later the Swiss Giuseppe Corradini and the shipyard where Filosa Stanislaus was built in 1818 and launched the Ferdinando I. the passage in close physical connection with industrial settlements of a bundle of tracks from the city center produced the effect tightening the nascent industries to the limits with the sea, and more and more isolated from the urban context have also reduced the whole coast from the Ponte della Maddalena to Pietrarsa, a reliquary of useless and abandoned factories.

The district remained independent until the 1925 when it was decreed the aggregation to the City of Naples along with Barra, Ponticelli and Capodichino. Affected by the so-called "Plan of the Suburbs" of 1980, was retrained on pre-existing settlement contextualized by landscapes of industrial elements obsolete and inextricably linked to the urban development along with the district "167" in Secondigliano and Scampia.

Fig.3.1: Aerial view of the old refineries Via Nuova Brecce of San Giovanni in Teduccio. Naples

In the period 1982-1990, there has been a gradual de-industrialization and nowadays the background looks like a cluster of industrial pavilions abandoned and dilapidated, there are numerous abandoned areas and houses are almost all of the old building . In the way of breccias, where there were tanks Agip and Q8, is today a *Rom* field.

In the neighborhoods of San Giovanni in Teduccio and Barra are concentrated over three hundred thousand people, on a 'area that is just over ten thousand square meters. And 'one of the poorest suburbs of Naples, where the high population density does not match an' adequate network of social services. The populous district is tight between the state of the Vesuvian towns, the highway Napoli-Salerno and is crushed by the harbor

The closure of many small and medium-sized companies has caused a lot of unemployment. Oil refineries do not require much labor. Many families are forced to survive on the 'economy of the alley. Very active smuggling of foreign cigarettes.

Affected by the so-called "Plan of the Suburbs" of 1980, was retrained on pre-existing settlement contextualized by landscapes of industrial elements obsolete and inextricably linked to the urban development along with the district "167" in Secondigliano and Scampia.

Fig.3.2: Aerial view of the Vigliena Touristic Port in San Giovanni in Teduccio. Naples.

Many and various are the issues related to the neighborhoods of Barra and San Giovanni. Industrial discharges current and past, the problem of legal and illegal spillage of waste, the many motorways in the vicinity of these areas make the air at very high risk for the health of the inhabitants of the districts of San Giovanni and Barra. The will of the City of Naples, together with the European Union funds aimed at the re-evaluation of an area as complex as it is rich in resources for the province of Naples, make the environmental monitoring of discharges and industrial fumes a priority for the quality of life of inhabitants of the districts San Giovanni and Barra.

It seems evident that the monitoring of industrial sites (water analysis, exhaust fumes, odors etc.) and neighboring residential areas is a necessity

dictated by common sense, not only scientific and ethical but especially in anticipation of the extension that suburbs will have in the coming decades and how the former industrial areas will be overlap in towns. Cases past and present as the **EX ITALISIDER** in Bagnoli (Na) and steelmaker **Ilva** of Taranto teach as monitoring and prevention are two key elements for safeguarding the health of man and the environment.

3.2 Sampling Site Characterization: L.A.S. Laboratory in *San Giovanni a Teduccio*.

This campaign of atmospheric particulate sampling was carried out in the period from 06.19.2013 to '08.01.2013, at the "LAS" Laboratory in Via Stefano Barbato. The sampler gravimetric was positioned on the roof of the laboratory for several reasons. The "L.A.S." laboratory is located near the motorway junction of the A3 Napoli-Pompei-Salerno. The area has an high vehicular traffic due to the presence of the commercial port in the southwest of the city of Naples.

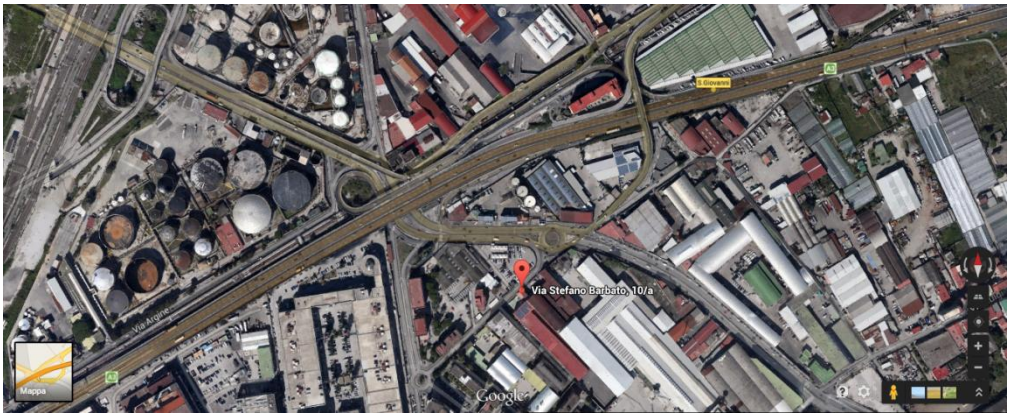


Fig.3.3 Google Maps View of LAS Laboratory (A) – Via Stefano Barbato n°10 San Giovanni A Teduccio – Naples.

To the north of the motorway junction are Agip and Q8 remains of tanks and deposits, respectively decommissioned in 1985 and in 1991 as a result

of arson.

Finally, to the southeast of the laboratory "LAS", on the coastline that runs from *Granilli* to *Pietrarsa*, there are numerous abandoned chimneys belonging to ENEL.

Although many of the old industrial productions are now disused areas listed above are currently home *Rom* fields and frequent are the uncontrolled fires from these areas.

In addition, although the industrial area of San Giovanni is a Teduccio for mainly abandoned, at north of the sampling site (and the highway) there is an active industrial area still served by a pipeline from the port of Vigliena (south) and arrives at refineries.

According to the specifics of the sampling area was decided to monitor and analyze the ambient air quality focus the attention on pollutants from vehicular traffic, smokestacks of the industrial area uncontrolled fires. Analytes covered in this PhD work were: PM_{10}, NO_x, SO_x, heavy metals, PAHs and inorganic component. The monitoring campaign of Atmospheric Particulate was the basis of our analysis and the main measure of comparison with data modeling.

It was conducted from June 19 to August 1, 2013. We were able to analyze 45 filters corresponding to 45 days of continuous sampling from 07:00 AM to 11:00 PM, from monday to sunday.

The filters of the period from 20th of June to 8th of July, 2013 were used for the determination of heavy metals and polycyclic aromatic hydrocarbons, while the filters of the period from 9th of July to 23th of July, 2013 were used for the determination of the inorganic ionic fraction of particulate matter.

3.3 Gravimetric Sampling for PM_{10}

The sampling was carried out by the gravimetric method with the sequential module for dust "Sentinel PM", combined with the sampler "Charlie", both branches "Tecora". The sampler consists of a sequential module Sentinel PM for the automatic replacement of the filters and provided with sampling head, for the cutting of particles to 10 μm, EPA approved type and sized to operate with a flow of 1 m^3/h. The sampling head is connected to a pump that a the air causes the atmospheric particulate impacts on the membrane inside the head and accedes. The activity of the pump is regulated by a control unit which, thanks to the action of a by-pass air valve brings to ensure a constant input.

Fig 3.4: Gravimetric Sampler "Sentinel PM + Charlie" by Tecora.

The Sentinel PM allows the automatic and sequential collection of atmospheric particles on membrane filters with a diameter of 47 mm, contained in special boxes holder. The autonomy of filters is of 16 units and allows to recover the sampled filters and replace them with white ones, without interrupting the sampling and without the need of human intervention.

The straight path of the suction tube and the separation of the zone of stay

of the filters from heat sources internal or radians, can raise and maintain the integrity of the samples. The filters used are cellulose fiber and quartz, the sampling head is equipped with a cascade impactor.

The gravimetric method (according to UNI EN 12341) consists of a filter in capturing particles suspended in a given volume of air to then determine the weight by weighing manual. This is a technique which allows to determine the concentration in terms of mass of volume (g/m^3) and is used for both PM_{10} and $PM_{2.5}$.

The sampling system consists of a sampling head having a diameter of 25 or 47 mm, in which is inserted a filter, a pump and a flow meter.

The membrane filter is composed of a rigid polymeric matrix, continuous and homogeneous, with a determined porosity at time of manufacture. The filters are chosen based on the analysis to be made. They may be Teflon, cellulose fiber or quartz fiber. While the filters in cellulose ester, having very smooth surfaces and homogeneous, are suitable for microscopic techniques, the quartz fiber filters are suitable for simple gravimetric measurements. Before sampling the filters are subjected to drying and weighed in the laboratory, brought on the field and placed in the sampler.

The sampler through a system input sucks atmospheric air at constant flow, here the suspended particulate matter is separated from an inertial impactor (or by a low-pressure impactor or by a micro holes impactor) consists of a series of parallel plates, exposed to flows faster for the narrowing of the sections of the gas, these dishes are gathering for inertia particles finer.

The flow lines of air are diverted abruptly exit in such a way that the particles larger than a certain diameter (diameter of the cut-off impactor) come from the flow lines and impinge on a collecting surface, while the smaller follow the stream lines.

Each stage cascade impactor collects its own range of particle sizes. in the sampler, the filter is held horizontally so that the flow is drawn from top to bottom, it is required to shelter from rain and bad weather (no moisture will be removed by drying).At the end of the sampling period of the filter is extracted from the sampler and to the repetition of the drying and the weighing, so as to determine the mass difference of PM10 collected.

The total volume of air sampled is calculated based on the value of the intake flow of the sampler and the duration of sampling. It is returned to the normal conditions of the reference (0 ° C, 101325 Pa) using the values of ambient temperature and pressure measured by the sampler.

The mass concentration of PM_{10} in the atmospheric air is calculated by dividing the total mass of the particles collected in the range in size of PM_{10} for the volume of air sampled, it is expressed in micrograms per cubic meter (mg/m^3).

Chapter 4.
"*Napoli Est*"Campaign: Experimental Results

4.1 Premise

The air quality monitoring campaign *"Napoli Est"* grew up from the partnership between the University of Naples Federico II and the Majority of the City of Naples aimed at the future realization of a sampling system and on-line monitoring of the ambient air of the newly created Metropolitan Region of Naples using sampling units of the Regional Environmental Protection of Campania (A.R.P.A.C.) and with data from the WRF-CAMx.
From the experimental point of view this PhD work is meant to represent the first step of the University of Naples Federico II toward the optimization of pre existing standard procedures for air pollutants analysis in order to increase the amount of chemical species analyzed and the quality of the obtained results. The monitoring was carried out according to the following schedule:

Polluttants	Period	Techniques	Ref. Procedure
PM_{10}	06/19 – 08/01 2013	Gravimetry	UNI-EN12341:2001
Heavy Metals	19/06 – 07/07 2013	Microwave Digestion + ICP-MS	UNI-EN14902:2005
PAHs	20/06 – 08/07 2013	Ultrasonic extraction + HPLC	UNI-EN15549:2005
Ionic Fraction	09/07 – 23/07 2013	Ultrasonic extraction + IC	-

Tab 4.1: Summary of the pollutants analyzed during the air monitoring campaign *"Napoli Est"*, period of monitoring, Techniques of analysis and reference procedures

Sampling and treatment of the filters was carried out at the **LAS** laboratory *"Environment & Health"* in the district of San Giovanni a Teduccio. **LAS** laboratory also hosted the gravimetric sampling. All chemical analysis were performed in the laboratory **ACE** - *Analytical Chemistry for the*

Environment by Prof. Marco Trifuoggi. The **ACE** lab is accredited to *ISO 9001: 2000* and *ISO / IEC 17025*.

4.2 Handling of filters and gravimetric results

The filters, both in quartz as in cellulose, used for sampling were previously inspected and weighed, placed in a dryer to remove any traces of humidity, and weighed until reaching a constant weight. Small filters were manipulated with blunt tweezers to avoid contamination or rubbing. A unique identifier was assigned to each of them, then they were placed in a labeled, sealed for storage and transportation container. Brought to the sampling site, filters were loaded in the sampler. The sampler was set according to the requirements appropriate of time of monitoring (21h) according to the industrial activities and vehicular traffic of the area and with a sample volume of 40 l/min. At the end of the sampling period, to withdraw the filters, they were brought in a transport containers uniquely marked for the subsequent transport to the laboratory.

It's necessary to record all details of each sample in the register of the filters, including the time of the stop, the air volume of the sample in cubic meters, mechanical or electrical interference during the sampling period and any other information that could be important for the assessment.

In the Figure 4.1 we report dates from the gravimetric sampling in the period from 19/06 to 01/07, 2013. The values in weight (shown in the graph in $\mu g/m^3$ of air sampled) show no violations of the limits of **Decree No. 155 / 2010** (50 $\mu g / m^3$ daily) with an average value found around 26 $\mu g/m^3$.

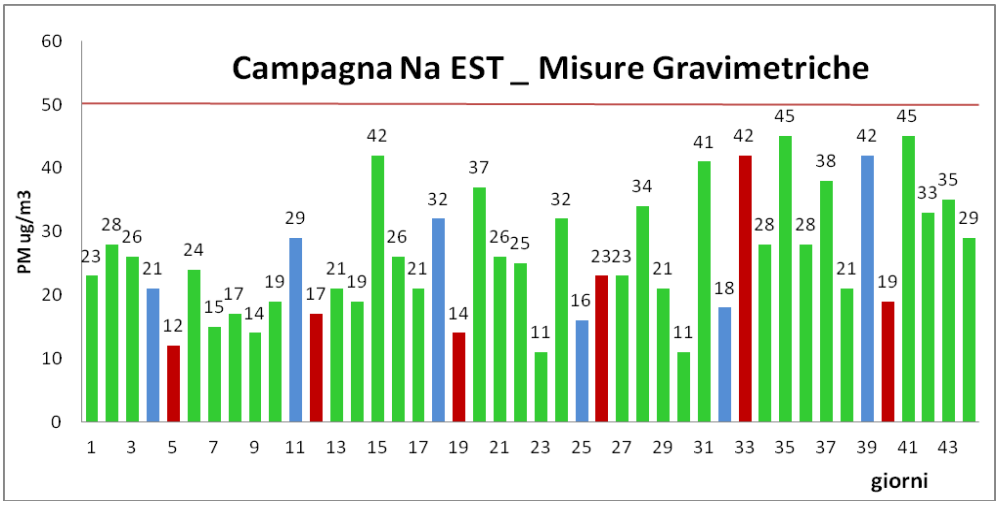


Fig 4.1: Results of the monitoring of air quality in the district of San Giovanni in Teduccio - former industrial area in the east side of Naples. The results were reported as follows: weekdays in green, Saturdays in blue, Sundays in red. The red line shows the law limit of 50 μg/m^3

4.3 Standard method for measuring concentration of Lead (Pb), Cadium (Cd), Arsenic (As) and Nichel (Ni) in the PM_{10} fraction of suspended particulate matter.

The European Standard specifies a method for the determination of particulate lead (Pb), cadmium (Cd), arsenic (As) and Nichel (Ni) as part of the PM_{10} aerosol, by microwave digestion of the samples and analysis by Inductively coupled plasma (quadrupole) mass spectrometer ICP-MS. The method gives fraction concentrations in the ranges listed in tab.4.2:

Metals	From (ng/m^3)	To (ng/m^3)
Lead (Pb)	1	4000
Cadmium (Cd)	0.1	50
Arsenic (As)	0.5	350
Nichel (Ni)	2	100

Tab. 4.2 Working ranges of the method in ng/m^3

Starting with the reference standard UNI EN 14902 we were able to determine simultaneously 20 heavy metals by acid digestion of the filters in quartz and cellulose used in the sampling process and subsequent analysis by ICP-MS.

4.3.1 Acid Digestion of Particulate Sampling Filters

Chemical analysis of particulate filters was carried out according to the procedure laid down by the UNI EN 14902. The process involves the adding of a mixture of 8 ml of nitric acid (HNO_3) and 2 ml of hydrogen peroxide (H_2O_2) in a 50 ml vessel where was inserted a filter of 47 mm of diameter in quartz or cellulose. The acid digestion takes place according to the following scheme: 1) heating ramp up to 180 ° C in 20 min. 2) Slow heating up to 220 ° C and then temperature holding for 20 minutes. After the digestion procedure the vessel were allowed to return to room temperature. Once cooled, the vessels sample solutions were transferred in a labeled volumetric flask containing ultrapure water brought to volume (50 ml) and analyzed ICP - MS.

4.3.2 Heavy Metals Determination by ICP-MS

The ICP-MS is an analytical technique generally used for the determinations of analytes in traces. It combines a source ICP (*inductively coupled plasma*) with a mass spectrometer. The ICP source is formed by a plasma torch, a radio frequency coil and a generator. The plasma torch, positioned horizontally at the center of the RF coil, generally consists of three quartz tubes. The argon, which is the gas typically used to generate the plasma, passes through the pipes with a flow rate of about 12-17 l/min. When the RF generator is operated, it produces an electromagnetic field. At

the gas passage through the torch, the RF generator applies a high voltage spark, causing some electrons drifting away from the argon atoms. These electrons, which are accelerated by the magnetic field, collide with other argon atoms, causing further ionization. This induced ionization continues with chain reactions, converting the gas into atoms, argon ions and electrons, forming the plasma. Most of the current applications of ICP-MS involves the analysis of liquid samples. There are several ways to introduce a liquid into the ICP-MS, but all reach the same result, the formation of an easily ionizable aerosol. The sample (liquid) is typically introduced at about 1 ml/min in the nebulizer using a peristaltic pump. The advantage of using a pump of this type is to ensure a constant flow of liquid irrespective of the difference in viscosity between the sample, standard and blank.

Once the sample reaches the nebulizer, the liquid goes down into aerosol thanks to the action of the pneumatic flow of the gas which converts the liquid particles into small droplets. Once the aerosol sample was introduced into the ICP torch, is completely de-solvated and towards the end of the torch is ionized. The ions formed by the ICP are typically positive ions, M^{+} or M^{2+}, therefore, elements which prefer to form negative ions, such as Cl^{-}, I^{-}, F, etc., are very difficult to determine. The ions must be transported to the mass spectrometer: through the interface region. It consists of two metal cones with the tiny holes in the middle (~ 1 mm), maintained under vacuum (1-2 torr) by a pump. The ions generated by the torch through the first cone, known as the *sampler cone*; from here run through a short distance until you come to the *skimmer cone*, generally smaller than the previous one. Because of the small diameters of the holes of the cones, the ICP-MS has some limitations for what concern the amount of dissolved solids in the samples.

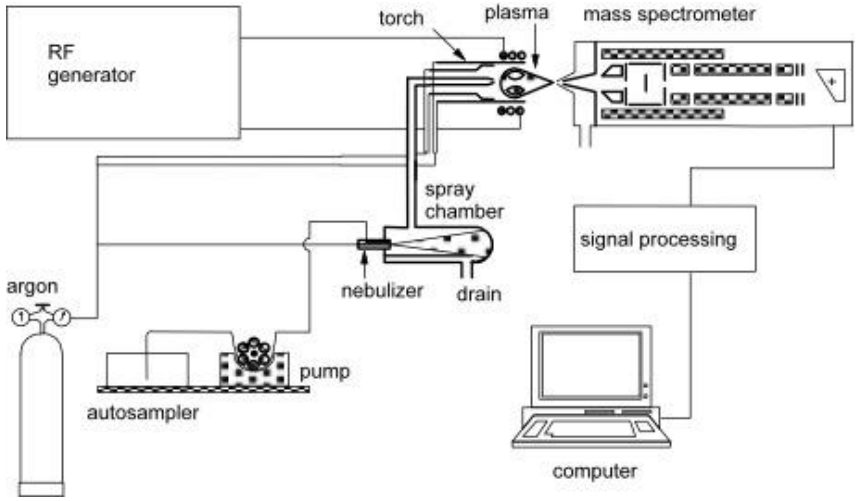


Fig. 4.2: General Scheme of an ICP-MS system **.**

In general, the samples must not contain more than 0.2% of total dissolved solids (TDS) for optimum performance of the instrument. If samples with very high levels of TDS would be inserted, the holes of the cones may become clogged, causing the decrease of sensitivity and detection capability of the instrument. The ions that emerge from the *skimmer cone* are conveyed in electrostatic plates, known as "*ionic lenses*", and led to the separation device of mass. The most commonly used type of mass spectrometer is a quadrupole mass filter. It is composed of four cylindrical rods of the same length and diameter. A quadrupole operates by placing both a field of radio frequency direct current (DC) or alternating current (AC) in opposite pairs of the four rods. Selecting the optimal ratio AC/DC on each pairs of rods, only certain ions with a specific mass / charge ratio will be allowed to cross the auction and reaching the detector, while the others will be expelled from the quadrupole. Since the ratio AC / DC can be adjusted very quickly, the quadrupole mass filter can separate up to 2400 amu (atomic mass unit) per second. This speed is the reason for which the

ICP-MS can simultaneously perform multi-elemental analysis. Once the ions have been separated according to their mass / charge ratio, must be counted by a suitable detector. One of the detector commonly used is the dynode electron multiplier. When an ion exceeds the quadrupole, proceeds along a curved path before impacting the first dynode. Once impacted frees an electron secondary. The arrangement of the dynode produces acceleration of these to the next dynode where secondary electrons are generated other electrons. This process is repeated for each dynode, generating a pulse of electrons that is finally captured by an anode. Aliquots of sample were diluted in the ratio 1: 3 with nitric acid (HNO_3) 1% v/v and later sent to ICP-MS. The ICP-MS analysis details are shown in table 4.2.

Parametet	Value(L/min)	Parameter	Value
Plasma flow	18	Sampling depth	7,5 mm
Auxiliary flow	1,8	RF Power	1,4 KW
Nebulizer flow	1	Stabilization delay	45 s

Tab 4.3: ICP-MS specific of work used in this work

4.3.3 Experimental Results

The results concerning the amount of twenty metals analyzed are shown in Table 4.4. There are no high concentrations of the heavy metals whose target values defined in the **Decree No. 155**, considering that the concentrations are below the detection limits of the instrument.

However in Figure 4.3 have been highlighted those metals whose concentration in the sampling period showed particular peaks. The metals in question are Barium, Boron, Iron, and Aluminium, characteristic of the vehicular traffic. For instance, Iron is a byproduct of the friction and wear of the brakes of the common drive. The inhalation of iron may contribute to

the formation of free radicals and induce oxidative processes in the human body whereas PM particles once reaching the pulmonary alveoli can cause from respiratory problems to other serious lung diseases. The largest source of airborne Aluminum containing particulates is the flux of dust from soil and the weathering of rocks and by volcanic activity Human activities, such as mining and agriculture, contribute to this wind-blown dust. The major anthropogenic sources of aluminum containing particulate matter include coal combustion, aluminum production, and other industrial activities, such as smelting, that process crustal minerals. Barium is a highly reactive metal that occurs naturally only in a combined state. The element is released to environmental media by both natural processes and anthropogenic sources.. Barium is released primarily to the atmosphere as a result of industrial emissions during the mining, refining, and production of barium and barium chemicals, fossil fuel combustion and rock dust into the air. In addition, coal ash, containing widely variable amounts of barium, is also a source of airborne barium particulates. Boron, is released into the atmosphere during volcanic eruptions; however, most is captured by the oceans. Coal-fired power plants and agricultural burning are major sources of atmospheric boron contamination. Boron compounds are released from anthropogenic sources such as coal-fired and geothermal steam power plants, chemical plants, and rockets as well as manufacturing facilities producing fiberglass and other products

ng/m³	Be	B	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Cd	Sn	Sb	Ba	Pb	Hg
Bl - Q	<0,1	<0,01	<0,01	<0,1	<0,1	<0,1	6,4	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	0,5	0,01	0,3	<0,1	<0,05
Bl - Ce	<0,1	<0,01	<0,01	<0,1	<0,1	<0,1	4,8	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	0,2	0,01	0,3	<0,1	<0,05
19/06	<0,1	3,75	58,85	3,1	<0,1	<0,1	58,9	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	<0,01	1,63	2,5	<0,1	<0,05
20/06	<0,1	10,23	58,17	2,2	<0,1	<0,1	43,2	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	1,05	2,04	33,6	<0,1	<0,05
21/06	<0,1	16,70	83,00	2,5	<0,1	0,2	64,4	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	<0,01	2,02	77,4	0,2	<0,05
22/06	<0,1	16,52	74,15	1,9	<0,1	0,3	61,3	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	1,05	1,57	81,2	<0,1	<0,05
23/06	<0,1	11,94	40,36	2,0	<0,1	<0,1	13,9	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	<0,01	0,91	80,4	<0,1	<0,05
24/06	<0,1	12,90	20,27	2,0	<0,1	<0,1	18,9	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	1,07	0,52	76,6	<0,1	<0,05
25/06	<0,1	15,40	46,10	1,9	<0,1	<0,1	23,4	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	<0,01	0,72	85,0	<0,1	<0,05
26/06	<0,1	16,96	67,91	1,2	<0,1	<0,1	53,2	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	1,07	1,13	83,6	<0,1	<0,05
27/06	<0,1	15,17	67,18	1,6	<0,1	<0,1	62,9	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	<0,01	0,93	95,9	<0,1	<0,05
28/06	<0,1	14,75	28,38	1,3	<0,1	<0,1	40,3	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	1,07	3,86	86,6	<0,1	<0,05
29/06	<0,1	17,54	80,54	0,8	6,1	<0,1	112,8	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	<0,01	1,26	84,2	0,7	<0,05
30/06	<0,1	15,12	104,42	1,1	<0,1	0,2	78,8	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	0,91	1,67	93,5	<0,1	0,11
01/07	<0,1	14,45	77,60	2,1	2,3	1,6	254,0	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	0,02	0,93	85,0	<0,1	<0,05
02/07	<0,1	13,98	59,10	2,3	<0,1	0,5	73,5	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	1,06	3,27	78,7	<0,1	<0,05
03/07	<0,1	52,45	163,67	3,5	25,3	<0,1	254,8	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	<0,01	3,52	353,9	<0,1	<0,05
04/07	<0,1	9,30	7,01	0,6	<0,1	<0,1	14,6	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	1,07	0,91	61,9	<0,1	<0,05
05/07	<0,1	15,38	82,79	0,5	<0,1	<0,1	58,8	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	<0,01	1,03	81,5	2,8	<0,05
06/07	<0,1	10,91	84,90	0,7	<0,1	4,5	344,8	<0,05	22,6	<5	<5	<0,5	<1	<1	10	<0,05	1,05	1,41	81,8	12,3	<0,05
07/07	<0,1	10,99	75,05	1,2	<0,1	<0,1	31,4	<0,05	<1	<5	<5	<0,5	<1	<1	<1	<0,05	<0,01	2,20	73,2	<0,1	<0,05

Tab.4.4: Heavy Metals determination in air sampling quartz and Cellulose Nitrate filters. All the filters were digested in acid mixture of Nitric Acid and Oxide Peroxide and analyzed by ICP-MS. All the results expressed in ng/m^3

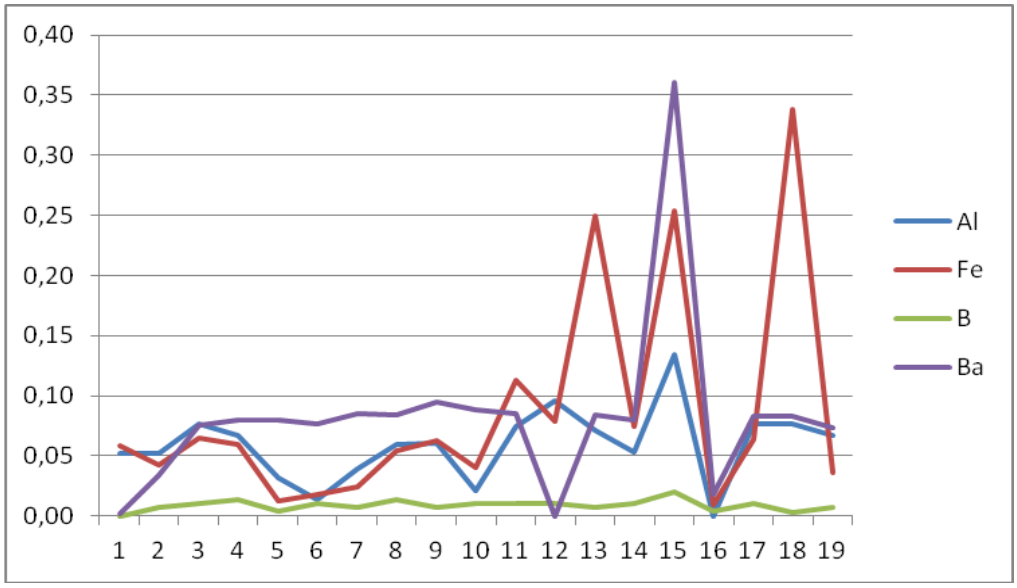


Fig.4.3: Focus of the results of the determination of metals in quartz filters and cellulose nitrate used in the sampling campaign. Concentration of the metals Fe, Al, B, Ba, measured in ng/m^3 according to the first nineteen sampling days.

4.4 Standard method for measuring concentration of Benzo [α] pyrene in ambient air.

Chemical analysis of particulate filters was carried out according to the procedure laid down by the UNI EN 15549. The standard specifies a measurement method for the determination of benzo[a]pyrene (BaP) in ambient air particle and describes the features and presentation criteria for the measurement method, when it is used as a reference method.

The measurement method chosen include: handling and preparation of filters, sampling of BaP as a fraction of PM_{10}, ultrasonic extraction of samples, analysis by HPLC (High Performance Liquid Chromatography) with fluorescence detection (FLD) and quantification. The method is applicable for measurements of BaP in the concentration range comprised, approximately, between 0.04 ng/m^3 and 20 ng/m^3.

4.4.1 Recovery test for ultrasonic bath extraction of PAHs

The Quantification of PAHs adsorbed on the filters used for sampling was not easy. The ultrasonic extraction, in fact, doesn't give quantitative guarantees as the acid digestion carried out on the filters intended for the analysis of heavy metals. The PAHs, in fact, are labile at temperature changes. It was, therefore, necessary to perform a recovery test of standard samples to verify the quantitative yield of the ultrasonic extraction process.

To quantify the possible presence of PAHs within our samples it is necessary, in advance, to introduce on a filter surface one internal Standard (constituent of the recovery test) at a known concentration containing the 15 PAHs and analyze it after extraction of the filter by ultrasonic bath and evaporation by Rotavapor. The experimental concentration of PAHs Mixture analyzed by HPLC are shown in Tab.4.2.

Species	HPLC results (ppm)
Naphtalhene	0,14965
Acenafthene	0,15182
Fluorene	0,16723
Phenanthrene	0,28355
Anthracene	0,02237
Fluoranthene	0,73992
Pyrene	0,31938
Benzo(a)anthracene	0,32019
Chrysene	0,39382
Benzo(b)fluoranthene	0,22278
Benzo(k)fluoranthene	0,28037
Benzo(a)pyrene	0,23818
Dibenzo(a,h)anthracene	0,01303
Benzo(g,h,i)perylene	0,19779
Indeno (1,2,3,c,d)pyrene	0,01102

Tab 4.5: summary of PAHs standard mixture concentrations analyzed by HPLC.

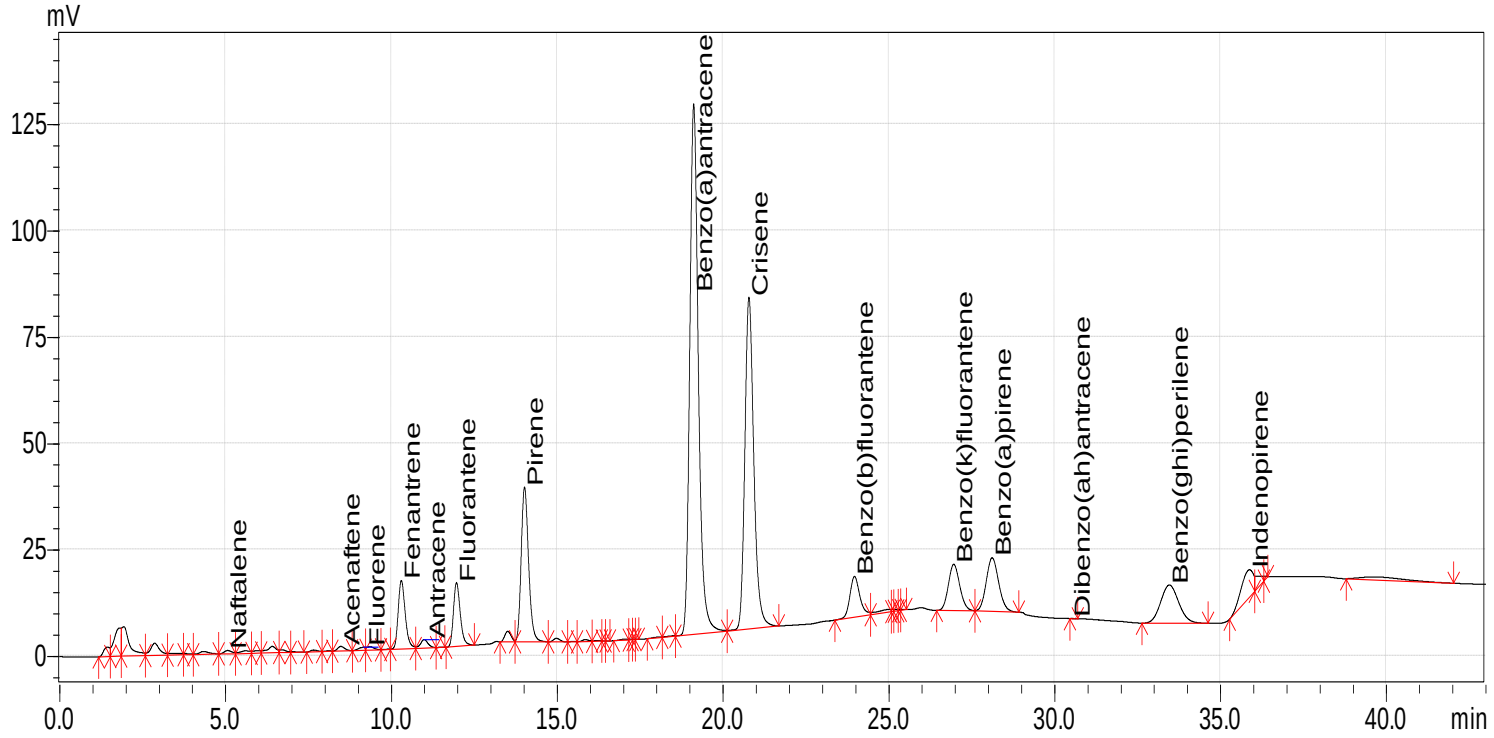


Fig 4.4: The HPLC chromatogram shows the results of recovery test performed on quartzum and cellulose filters. Detection Limit = 0.02 µg/mL 0.2 µg/m^3. Monitoring Period: from 20.06.13 to 09.07.13 at LAS Laboratory – San Giovanni a Teduccio (Na)

The HPLC chromatogram in figure 4.4 shows the retention times for the15 PAHs analyzed.

The concentration of this mixture standard obtained from HPLC (shown in Tab.4.5 and in the relative chromatogram in Fig.4.4) was taken as point of reference of our recovery test. Starting from the standard mixture consisting of 15 PAHs, we focused our attention on six PAHs in particular considered possible carcinogens or probable carcinogens by the *International Agency for Research on Cancer* (Fig.4.5).

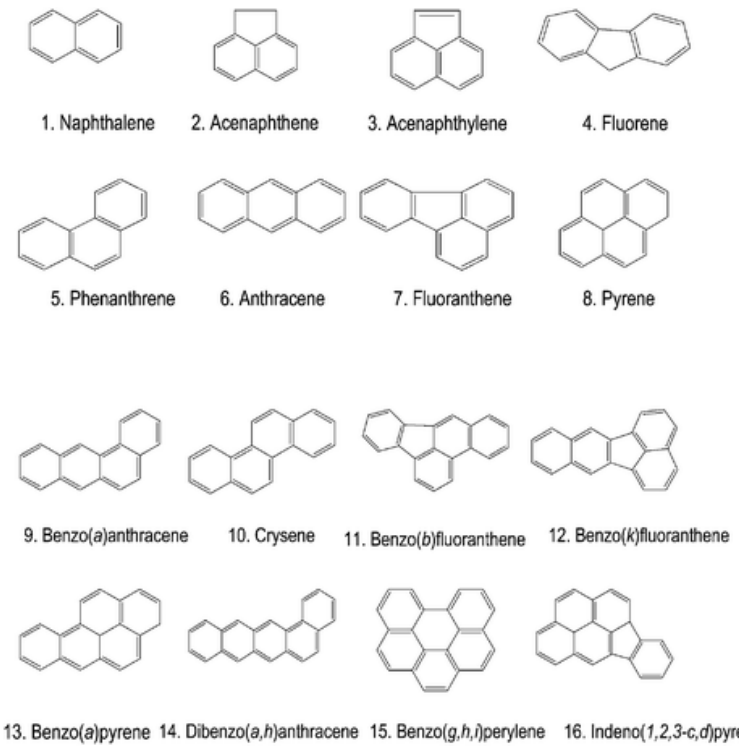


Fig 4.5: IARC (*International Agency for Research on Cancer* – www.iarc.fr) PAHs classification: carcinogenic and potential carcinogens PAHs are: 13.Benzo(a)pyrene (2A); 9.Benzo(a)anthracene (2A); 11.Benzo(b)fluoranthene (2B); 12.Benzo(k)fluoranthene (2A); 14.Dibenzo(a,h)anthracene (2B); 16.Indeno(1,2,3-cd)pyrene (2B) where: 2A means probable carcinogens and 2B means possible carcinogens) [3]

Each filter (one for type) was tabled an aqueous solution containing a mixture

of the 6 PAHs standards before mentioned with a concentration of 250 ppm. The filters have undergone to the same conditions of extraction, sonication and evaporation in a rotavapor of the normal samples. After all, the solutions were tested at HPLC. The rate of recovery (Tab 4.6) obtained found to be about 80-95% except for the Dibenzo(a,h)anthracene.

	Blank_Q	Blank_C	Recovery test_PAH Mix	Recovery
Species	**(μg/m³)**	**(μg/m³)**	**(μg/m³)**	**(%)**
Benzo(a)anthracene	<0,2	<0,2	2,39	**93,1**
Benzo(b)fluoranthene	<0,2	<0,2	2,33	**89,1**
Benzo(k)fluoranthene	<0,2	<0,2	2,39	**93,1**
Benzo(a)pyrene	<0,2	<0,2	2,46	**97,3**
Dibenzo(a,h)anthracene	<0,2	<0,2	0,15	**5,2**
Indeno (1,2,3,c,d)pyrene	<0,2	<0,2	2,06	**80,4**

Tab 4.6: Ultrasonic Bath extraction recovery test results.

4.4.2 Ultrasonic extraction of samples

We proceed to sample preparation by extraction with an organic solvent, dichloromethane (CH_2Cl_2). The filters were placed in a beaker and dissolved in 4 ml of CH_2Cl_2.The samples were placed in an ultrasonic bath to make a sonication of 15 minutes. At the end of the ultrasonic extraction the extracts were collected into a tube. The operation was repeated 3 times on the same filter, collecting the extract in the same test tube, up to, then, for a total of about 12 ml of solvent for each filter. The samples were dryed to the Rotavapor, thus it proceeds to removal of the solvent by evaporation at low pressure. Once completed removal procedure of the solvent , every sample was recovered by a Gilson.

4.4.3 PAHs' parallel determination by HPLC

Figure 4.4. presents the results of the analyzes of PAHs on individual daily

samples (19 days) by HPLC. Examining the indicator proposed in the legislation, it is immediately evident that the time scale for a proper assessment is generally one year. A measurement campaign conducted for a shorter period may be useful in view of preliminary approach to the characterization of the emission levels in the area subject to the investigation. However, the concentrations of PAHs have a marked seasonal pattern and in spring and summer months will generally have concentrations below the sensitivity analysis. In part this is due to a decrease of the sources present, to weather conditions which favor the diffusion of pollutants capable of activating reactions of degradation of PAHs The IPA containing 4 rings, or fewer, generally remain in gaseous form when released into the atmosphere. After stationed less than 24 hours in the outdoor air degrade in response to a sequence of reactions. The most important source of emission of PAHs is that of internal combustion engines fueled by gasoline and diesel fuel. Other sources of emissions are represented by heating systems powered by fuel oil (Benzo-naphtho-Thiophene, Benzo (a) anthracene) and Chrysene, power plants, refineries, plants tarring, waste incineration, exhaled smoke from the burning of wood and from other combustion processes in which the carbon in the fuel is not completely converted to CO and CO_2. Analysis of the graph shows, first, a percentage of Naphthalene than other IPA. The Naphthalene is the most volatile, with a vapor pressure of 10.9×10^{-5} bar at room temperature, while the benzo [a] pyrene is one of the less volatile having a vapor pressure equal to $8,4x10^{-12}$ bar at room temperature.

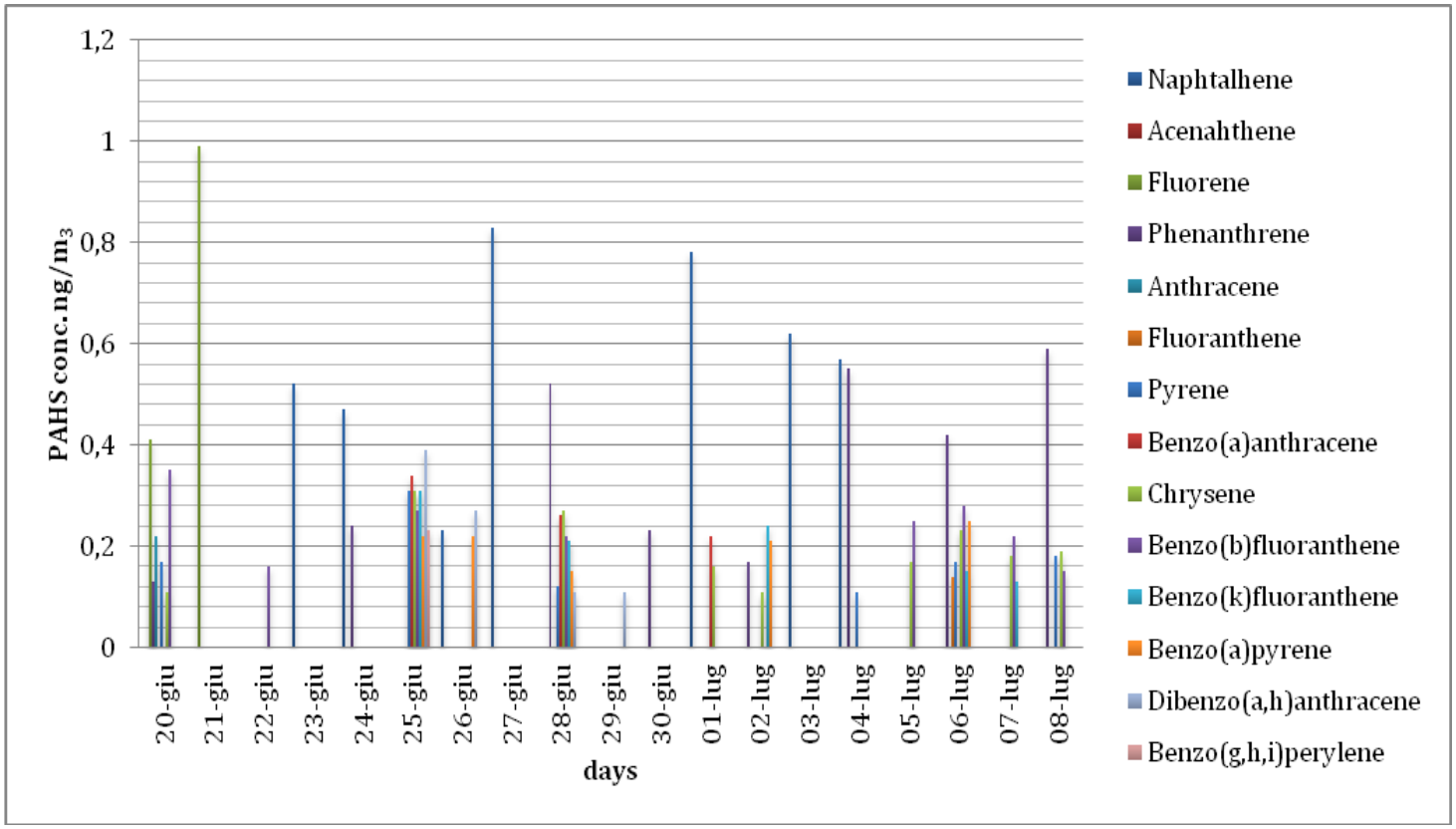


Fig. 4.6: Graphic of the concentration of PAHs in filter used for Particulate Matter PM10 sampling campaign. The detection limit is 0,04 ng/m^3.

	20/6	21/6	22/6	23/6	24/6	25/6	26/6	27/6	28/6	29/6	30/6	01/7	02/7	03/7	04/7	05/7	06/7	07/7	08/7
Naphtalhene	<0,04	<0,04	<0,04	0,52	0,47	<0,04	0,23	0,83	<0,04	<0,04	<0,04	0,78	<0,04	0,62	0,57	<0,04	<0,04	<0,04	<0,04
Acenahthene	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04
Fluorene	0,41	0,99	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04
Phenanthrene	0,13	<0,04	<0,04	<0,04	0,24	<0,04	<0,04	<0,04	0,52	<0,04	0,23	<0,04	0,17	<0,04	0,55	<0,04	0,42	<0,04	0,59
Anthracene	0,22	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04
Fluoranthene	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	0,14	<0,04	<0,04
Pyrene	0,17	<0,04	<0,04	<0,04	<0,04	0,31	<0,04	<0,04	0,12	<0,04	<0,04	<0,04	<0,04	<0,04	0,11	<0,04	0,17	<0,04	0,18
Benzo(a)anthracene	<0,04	<0,04	<0,04	<0,04	<0,04	0,34	<0,04	<0,04	0,26	<0,04	<0,04	0,22	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04
Chrysene	0,11	<0,04	<0,04	<0,04	<0,04	0,31	<0,04	<0,04	0,27	<0,04	<0,04	0,16	0,11	<0,04	<0,04	0,17	0,23	0,18	0,19
Benzo(b)fluoranthene	0,35	<0,04	0,16	<0,04	<0,04	0,27	<0,04	<0,04	0,22	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	0,25	0,28	0,22	0,15
Benzo(k)fluoranthene	<0,04	<0,04	<0,04	<0,04	<0,04	0,31	<0,04	<0,04	0,21	<0,04	<0,04	<0,04	0,24	<0,04	<0,04	<0,04	0,15	0,13	<0,04
Benzo(a)pyrene	<0,04	<0,04	<0,04	<0,04	<0,04	0,22	0,22	<0,04	0,15	<0,04	<0,04	<0,04	0,21	<0,04	<0,04	<0,04	0,25	<0,04	<0,04
Dibenzo(a,h)anthracene	<0,04	<0,04	<0,04	<0,04	<0,04	0,39	0,27	<0,04	0,11	0,11	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04
Benzo(g,h,i)perylene	<0,04	<0,04	<0,04	<0,04	<0,04	0,23	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04
Indeno (1,2,3,c,d)pyrene	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04

Tab.4.7: PAHs determination in air sampling quartz and Cellulose Nitrate filters. The PAHs were extracted from filters by ultrasonic bath and Rotavapor. The solutions were and analyzed by HPLC. All the results expressed in ng/m^3

Significant concentrations of B(a)P were detected only in 5 days of sampling, but are not found to be higher than the target air quality equal to 1 ng/m^3. Among the fuel for civilian use we note the impact on emissions of Benzo(a)pyrene firewood.

The presence of benzo(a)anthracene and Chrysene, albeit in trace amounts, is an indicator of pollution sources from heating systems powered by fuel oil.

As there are no obvious peaks indeno(1,2,3,cd)pyrene (below the threshold of detection of the method) and Benzo(g,h,i)perylene compared to Benzo(a)pyrene, it was not possible to assume the prevalence of urban pollution by emissions from combustion relative to the entire measurement campaign.

4.5 Parallel determination of Inorganic Fraction in Particulate Matter PM10 by ultrasonic extraction in ultrapure water and Ion Chromatography.

Suspended particulate matter (SPM) in air generally is considered to be all airborne solid and low vapor pressure liquid particles, involving a complex, multi-phase system consisting of a spectrum of aerodynamic particle sizes ranging from below 0.01 μm to 100 μm and larger. Historically, particulate matter (PM) measurement has concentrated on total suspended particulates (TSP), with no preference to size selection. Researchers generally recognize that these particles (2.5 μm their retention time in the air parcel is shorter than the fine particle fraction. Recent studies involving particle transport and transformation strongly suggest that atmospheric particles commonly occur in two distinct modes: the fine and the coarse. The fine or accumulation mode (also termed the breathable particulate matter) is attributed to growth of particles from the gas phase and subsequent agglomeration, while the coarse mode is made of mechanically abraded or ground particles. Particles that have

grown from the gas phase (either because of condensation, transformation, or combustion) occur initially as very fine nuclei--0.05 μm. These particles tend to grow rapidly to accumulation mode particles around 0.5 μm, which are relatively stable in the air. Because of their initially gaseous origin, particle sizes in this range include inorganic ions such as sulfate, nitrate, ammonia, combustion-form carbon, organic aerosols, metals, and other combustion products. Coarse particles, on the other hand, are produced mainly by mechanical forces such as crushing and abrasion. Pollen and spores also inhabit the coarse particle range, thus providing dominance by materials of geological origin. Coarse particles, therefore, normally consist of finely divided minerals such as oxides of aluminum, silicon, iron, calcium, and potassium. Coarse particles of soil or dust mostly result from entrainment by the motion of air or from other mechanical action within their area. Since the size of these particles is normally >2.5 μm their retention time in the air parcel is shorter than the fine particle fraction.

The chemistry of pollutants in the atmosphere and their natural propensity to nucleation, accumulation and removal (dry or wet) make the troposphere a "reaction environment" difficult to analyze. Unlike the organic component of the atmospheric particulate, labile effect of temperature and of the natural degradation over time, the inorganic component of the atmospheric particulate PM_{10} may represent a fingerprint of the average composition of the particulates.

In this PhD work, we have defined a method for the parallel determination of the ionic fraction - anionic and cationic – of particulate air pollution PM_{10} starting from the filters used in the sampling phase.

As in the previous case involving the determination of PAHs also in this case, for the extraction of the inorganic fraction of the particulate has been used an ultrasonic bath. To evaluate the percentage of recovery of this step was

performed, a recovery test with standard of known concentration.

4.5.1 Recovery test for ultrasonic bath extraction of inorganic fraction of PM_{10}

To assess the percentage recovery of the ultrasonic bath have been taken into account the following variables: the composition of the filters used, the time of sonication and the percentage recovery as a function of time. Filters of different composition - quartz, cellulose nitrate and PTFE - generally used in the sampling phases of the ambient air and a white of each. Each filter was impregnated with 100 μL of each standard anions and cations. For each addition, the filter was placed in a desiccator so as to evaporate all the water before proceeding to the next standard.

The standards were added in order: F^-; Cl^-; Br^-; SO_4^{2-} for anionic fraction and Na^+; K^+; Mg^{2+}; Ca^{2+} for the cationic fraction.

The filters at this point have been inserted within plastic flasks. Were added 10 ml of ultrapure water (Cond = 0.0056 μS/cm) for weighing and each flask was covered with parafilm. The sonication was performed at different times (t = 30 min, 45 min, 60 min, 90 min) to evaluate the percentage of recovery of ions in solution.

The results have shown that for periods of less than 45 minutes the extraction is not complete. On the other hand the sonication performed on time than 60 minutes results in the slow loss of consistency of the filters which in part are dispersed in solution making subsequent chromatographic analysis untrusted. In Tab 4.8 and 4.9 we show the results of recovery test performed on quartz, nitrate cellulose and PTFE filters for the anionic fraction (fluorides, chlorides, sulfates and bromides) and for the cationic fraction (Sodium, Potassium, Calcium and Magnesium) of particulate matter $PM_{10.}$

Yield	Quartz	Cellulose	PTFE
t=45 min		(%)	
F^-	79	84	51
Cl^-	99	100	2
Br^-	98	100	5
SO_4^{--}	100	100	74

Tab. 4.8: results of recovery test of anionic fraction of particulate matter PM_{10} performed on quartz, cellulose nitrate and PTFE filter for 45 minutes by ultrasonic bath in ultra pure water Cond = 0.0056 uS/cm

Yield	Quartz	Cellulose	PTFE
t=45 min		(%)	
Na^+	98	95	51
K^+	94	79	74
Ca^{2+}	83	81	64
Mg^{2+}	84	84	6

Tab. 4.9: results of recovery test of cationic fraction of particulate matter PM_{10} performed on quartz, cellulose nitrate and PTFE filter for 45 minutes by ultrasonic bath in ultra pure water Cond = 0.0056 uS/cm

Considering the results of tests of recovery we decided to focus our attention on the filters in the fourth and cellulose nitrate, which have made more high subjecting sample filters under the same conditions of extraction of 45 minutes in ultrapure water.

4.5.2 Ultrasonic extraction of samples

Were taken into consideration the filters from the monitoring campaign in east Naples time period from 07.09.2013 to 07.23.2013. The filters used were in quartz and cellulose nitrate. Each filter was placed in a plastic flask and were added 10 ml of ultrapure water with a conductivity of 0.0056 μS/cm. The sonication was performed in a ultrasonic bath for 45 minutes.

After sonication, the solution was recovered in plastic tubes and stored in the refrigerator, away from sources of light at a temperature of 4 °C. The samples

were then transferred to the ion chromatograph for qualitative and quantitative analysis.

4.5.3 Inorganic Fraction of PM_{10}:parallel determination by Ion Chromatography.

The results of the quantitative and qualitative inorganic fraction of particulate air pollution are shown in Figures 4.7 and 4.8. The Anionic Fraction of PM results composed mainly by sulphates and nitrates. The largest natural direct source of sulphates are volcanic eruptions. Major volcanic eruptions which inject sulfur dioxide into the stratosphere are the dominant source of sulfuric acid aerosol in the stratosphere. Aerosols formed from coal combustion have a high concentration of sulfates at the surface. This occurs because sulfates condense late, concentrating on the surface. Sulphates concentrations increase with decreasing particle size. Some of the sulfate associated with the aerosols is in the form of sulfuric acid. The possible origin of these compound can be redirected to the proximity of the Volcano *Vesuvium*. On the other hand, atmospheric ammonia contributes to the formation of aerosol nitrate, an important constituent of inorganic fine particulate matter, and atmospheric ammonia is a significant source of acidification and excess nutrient loading to sensitive ecosystems. Nitrates are also indicative of the presence of possible fires in the area and to vehicular pollution.

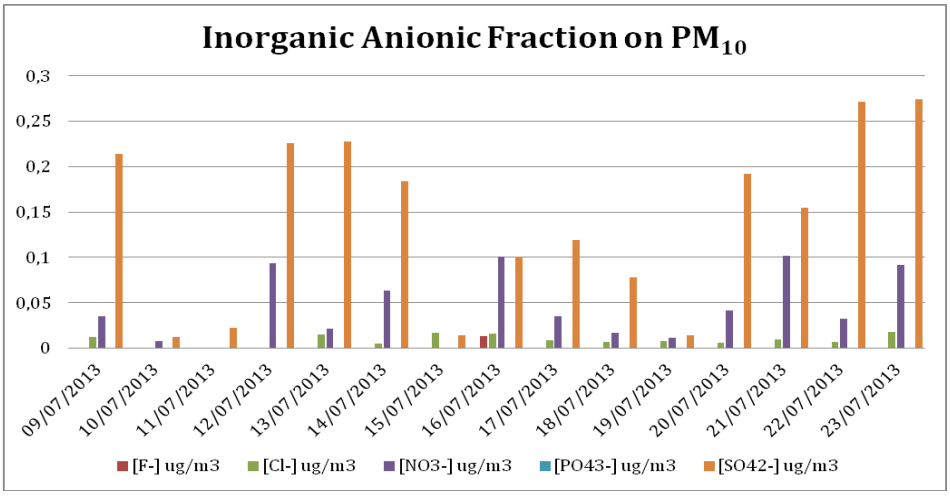


Fig.4.7: Graph of the variation in concentrations of inorganic anions contained in atmospheric particulate PM_{10} during the sampling days. The concentrations were determined by extraction in ultrasonic bath and subsequent analysis by ion cromatography . Detection limit = 0.003 μg / m^3

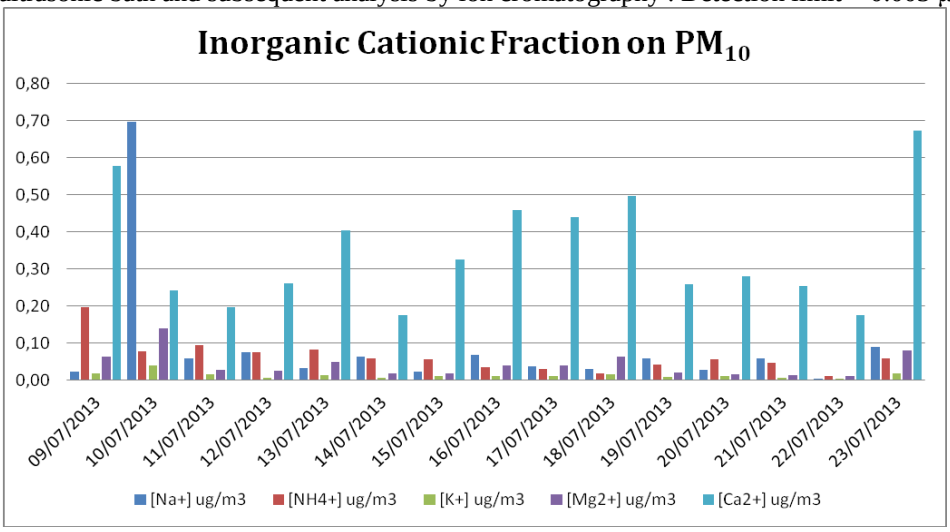


Fig.4.8: Graph of the variation in concentrations of inorganic anions contained in atmospheric particulate PM_{10} during the sampling days. The concentrations were determined by extraction in ultrasonic bath and subsequent analysis by ion cromatography . Detection limit = 0.003 μg / m^3

The Cationic Fraction of PM is mainly composed by Sodium and Calcium. The presence of Sodium can be redirect to the proximity of the sea. The presence of sodium is a constant of the chemical composition of the atmosphere of the city of Naples for the presence of the coast a few kilometers from the sampling area

and more specifically the Port of Vigliena. On the other hand the presence of calcium can be due to the presence of some dismissed building near sampling area. The district of San Giovanni in Teduccio, in fact, began as the industrial district and productive but it has seen over the last 30 years, a staggering increase of housing complexes that have been built near the now abandoned and dilapidated old factories. Around the sample were in fact two abandoned buildings and in the process of demolition and reuse of the area

	[F^-] ug/m^3	[Cl^-] ug/m^3	[NO_2^-] ug/m^3	[NO_3^-] ug/m^3	[PO_4^{3-}] ug/m^3	[SO_4^{2-}] ug/m^3	[Na^+] ug/m^3	[NH_4^+] ug/m^3	[K^+] ug/m^3	[Mg^{2+}] ug/m^3	[Ca^{2+}] ug/m^3
09/07/2013	< 0,003	0,012	< 0,003	0,04	< 0,003	0,21	0,02	0,20	0,02	0,06	0,58
10/07/2013	< 0,003	< 0,003	< 0,003	0,01	< 0,003	0,01	0,70	0,08	0,04	0,14	0,24
11/07/2013	< 0,003	< 0,003	< 0,003	< 0,003	< 0,003	0,02	0,06	0,09	0,02	0,03	0,20
12/07/2013	< 0,003	< 0,003	< 0,003	0,09	< 0,003	0,23	0,08	0,08	0,01	0,03	0,26
13/07/2013	< 0,003	0,02	< 0,003	0,02	< 0,003	0,23	0,03	0,08	0,01	0,05	0,40
14/07/2013	< 0,003	0,01	< 0,003	0,06	< 0,003	0,18	0,06	0,06	0,01	0,02	0,18
15/07/2013	< 0,003	0,02	< 0,003	< 0,003	< 0,003	0,01	0,02	0,06	0,01	0,02	0,33
16/07/2013	0,013	0,02	< 0,003	0,10	< 0,003	0,10	0,07	0,03	0,01	0,04	0,46
17/07/2013	< 0,003	0,01	< 0,003	0,04	< 0,003	0,12	0,04	0,03	0,01	0,04	0,44
18/07/2013	< 0,003	0,01	< 0,003	0,02	< 0,003	0,08	0,03	0,02	0,02	0,06	0,50
19/07/2013	< 0,003	0,01	< 0,003	0,01	< 0,003	0,01	0,06	0,04	0,01	0,02	0,26
20/07/2013	< 0,003	0,01	< 0,003	0,04	< 0,003	0,19	0,03	0,06	0,01	0,02	0,28
21/07/2013	< 0,003	0,01	< 0,003	0,10	< 0,003	0,15	0,06	0,05	0,01	0,01	0,25
22/07/2013	< 0,003	0,01	< 0,003	0,03	< 0,003	0,27	< 0,003	0,01	< 0,003	0,01	0,18
23/07/2013	< 0,003	0,02	< 0,003	0,09	< 0,003	0,27	0,09	0,06	0,02	0,08	0,67

Tab 4.10: Summary table of the concentrations of inorganic anions and cations contained in atmospheric particulate PM_{10} determined by extraction in ultrasonic bath and subsequent analysis by ion chromatography. Detection limit = 0.003 μg / m^3

4.6 Conclusions

The air quality monitoring campaign *"Naples–Est"* has covered a total of 53 days of gravimetric sampling of atmospheric particulate PM_{10}. There were no exceedances of the annual limit of 50 $\mu g/m^3$ with a daily average of 26 $\mu g/m^3$.

Starting from the filters used for gravimetric sampling was carried out a quantitative and qualitative analysis of the metallic component (optimizing the procedure UNI EN 14902 for the simultaneous analysis of 20 metals), the organic component and in this case the optimization of the procedure UNI EN 15549 for the determination of benzo [a] pyrene being able to simultaneously determine 15 PAHs.

As regards the analysis of the inorganic component - the anionic and cationic - contained in the atmospheric particulate PM_{10} has been developed a method for the parallel determination of anions and cations by extraction in ultrapure water using ultrasonic bath, and subsequent analysis by ion chromatography.

Chapter 5
Models for Air Quality Improvement

5.1 Introduction

The analysis of air quality is a discussion topic increasingly followed within the scientific communities around the world. The complexity of the atmosphere as "reaction environment" with the effects of meteorology on air chemistry necessary coupling the traditional methods of sampling and chemical - physical analyzes with predictive models of chemistry and transport of air pollutants.

In this PhD project was developed a system of three programs for compilation and verification of the three main calculation modules to the base of the modeling system: the geographical pattern, the emission model, and the model of chemistry and transport. In a second phase it a three-dimensional meteorological models for the definition of the geographical pattern centered on the Gulf of Naples was defined, and was finally developed the date set system for pollutant emissions for the definition of a model centered on the calculation grid of the Gulf of Naples.

The project was developed in collaboration with the City of Naples is the basis for the future development of a prognostic model on line for determining air quality useful to the citizens of the entire metropolitan area of Naples.

5.2 WRF – *Weather Research and Forecasts*[4]

The WRF project has developed a next-generation mesoscale forecast model and assimilation system to advance both the understanding and the prediction of mesoscale precipitation systems and to promote closer ties between the research and operational forecasting communities. With the release of WRF version 2.0 to the community in May of 2004, the wide dissemination of the WRF modeling system to a large number of users and its application in a variety of areas including storm-scale research and prediction, air-quality modeling, wildfire simulation, hurricane and tropical storm prediction, regional climate, and operational numerical weather prediction are well underway.

Operational implementation of WRF is underway at the NOAA National Centers for Environmental Prediction and at the U.S. Air Force Weather Agency. A joint NOAA/NCAR/DoD Developmental Testbed Center has been formed to facilitate the ongoing testing, evaluation, and transition of new developments from the research community into operations at NCEP, AFWA, and at the U.S. Navy through Operational Testbed Centers being established at the respective centers. The WRF system consists of the WRF model itself, preprocessors for producing initial and lateral boundary conditions for idealized, real-data, and one-way nested forecasts, postprocessors for analysis and visualization, and a three-dimensional variational data assimilation. The WRF Model contains two dynamical cores, providing additional flexibility across institutions and applications. The NCAR-developed Advanced Research WRF (ARW; originally the Eulerian Mass, or "EM" core) uses a time-split high-order Runga-Kutta method to integrate a conservative formulation of the compressible non-hydrostatic equations. ARW is supported to the research community as WRF Version 2 and is undergoing operational implementation at the U.S. Air Force Weather Agency.

NOAA/NCEP's operational implementation of WRF is using dynamics adapted to the WRF ASF from the Non-hydrostatic Mesoscale Model (NMM).

The following figure shows the flowchart for the WRF Modeling System Version 3.

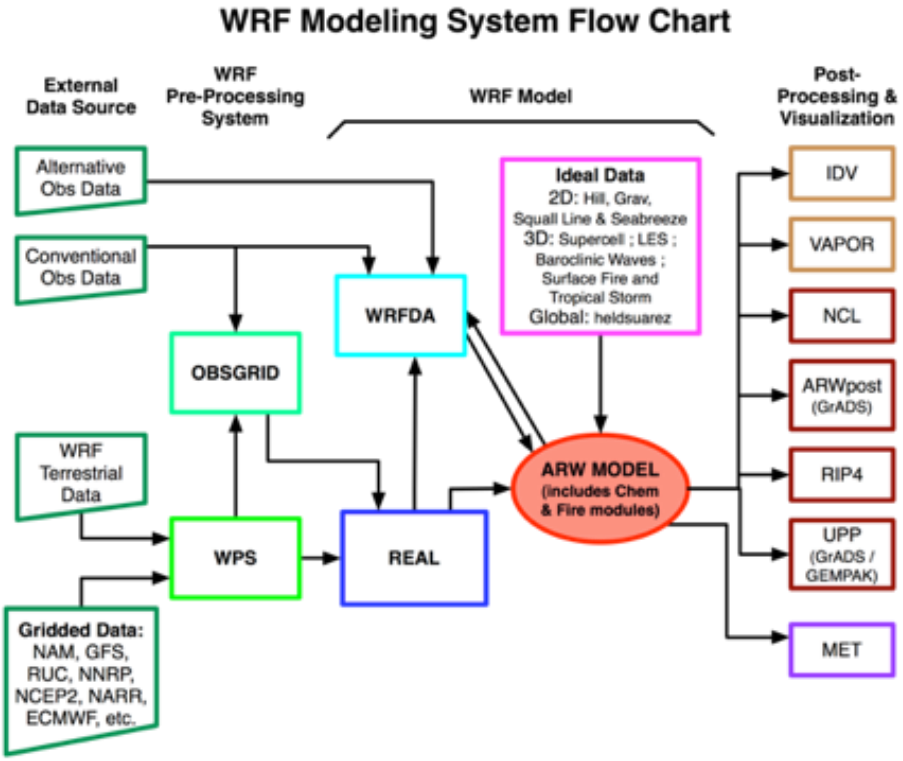


Fig. 5.1: General Flow chart of WRF. The scheme shows all the main component of WRF from the pre-processing system to the outputs.

As shown in the diagram, the WRF Modeling System consists of these major programs:

- WPS - The WRF Preprocessing System
- WRF
- GrAds - Post-processing & Visualization tools

5.2.1 WPS - *The WRF Preprocessing System*

This program is used primarily for real-data simulations. Its functions include 1) defining simulation domains; 2) interpolating terrestrial data (such as terrain, landuse, and soil from another model to this simulation domain. Its main features include:

- GRIB 1/2 meteorological data from various centers around the world
- USGS 24 category and MODIS 20 category land datasets; USGS GTOPO30

elevation dataset; Global 5-minutes United Nation FAO, and North-America STATSGO 30 sec soil category dataset; 10-min greenness fraction data based on AVHRR and 30-sec greenness fraction data based on 10 years MODIS; MODISbased leaf-area index; 0.15 degree monthly albedo and snow albedo data; and 1-degree deep soil temperature data; plus a few specialized datasets

- Map projections for 1) polar stereographic, 2) Lambert-Conformal, 3) Mercator and 4) latitude-longitude
- Nesting
- User-interfaces to input other static data as well as met data

The WRF Preprocessing System (WPS) is a set of three programs whose collective role is to prepare input to the *real* program for real-data simulations. Each of the programs performs one stage of the preparation: *geogrid* defines model domains and interpolates static geographical data to the grids; *ungrib* extracts meteorological fields from GRIB formatted files; and *metgrid* horizontally interpolates the meteorological fields extracted by ungrib to the model grids defined by geogrid. The work of vertically interpolating meteorological fields to WRF eta levels is performed within the *real* program.

The data flow between the programs of the WPS is shown in the figure above. Each of the WPS programs reads parameters from a common namelist file, as shown in the figure. This namelist file has separate namelist records for each of the programs and a shared namelist record, which defines parameters that are used by more than one WPS program.

The WPS consists of three independent programs: geogrid, ungrib, and metgrid. Also included in the WPS are several utility programs, which are described in the section on utility programs. A brief description of each of the three main programs is given below, with further details presented in subsequent sections.

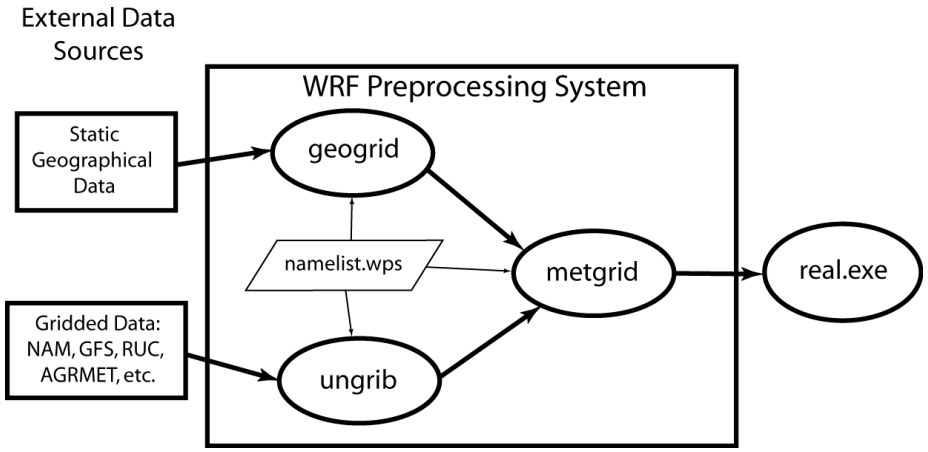


Fig. 5.2: Flow chart of WPS – WRF Pre-processing System. The scheme shows all the main component of WPS: geogrid, ungrib, metgrid and real.

The purpose of **Geogrid** is to define the simulation domains, and interpolate various terrestrial data sets to the model grids. The simulation domains are defined using information specified by the user in the "geogrid" namelist record of the WPS namelist file, namelist.wps. In addition to computing the latitude, longitude, and map scale factors at every grid point, geogrid will interpolate soil categories, land use category, terrain height, annual mean deep soil temperature,

monthly vegetation fraction, monthly albedo, maximum snow albedo, and slope category to the model grids by default. Global data sets for each of these fields are provided through the WRF download page, and, because these data are time-invariant, they only need to be downloaded once. Several of the data sets are available in only one resolution, but others are made available in resolutions of 30", 2', 5', and 10'; here, " denotes arc seconds and ' denotes arc minutes. The user need not download all available resolutions for a data set, although the interpolated fields will generally be more representative if a resolution of data near to that of the simulation domain is used. However, users who expect to work with domains having grid spacing that cover a large range may wish to eventually download all available resolutions of the static terrestrial data.

The **Ungrib** program reads GRIB files, "*degribs*" the data, and writes the data in a simple format called the intermediate format (see the section on writing data to the intermediate format for details on the format). The GRIB files contain time-varying meteorological fields and are typically from another regional or global model, such as NCEP's NAM or GFS models. The ungrib program can read GRIB Edition 1 and, if compiled with a "GRIB2" option, GRIB Edition 2 files. GRIB files typically contain more fields than are needed to initialize WRF. Both versions of the GRIB format use various codes to identify the variables and levels in the GRIB file. Ungrib uses tables of these codes – called Vtables, for "variable tables" – to define which fields to extract from the GRIB file and write to the intermediate format. Details about the codes can be found in the WMO GRIB documentation and in documentation from the originating center. Vtables for common GRIB model output files are provided with the ungrib software. Vtables are provided for NAM 104 and 212 grids the NAM AWIP format, GFS, the NCEP/NCAR Reanalysis archived at NCAR, RUC (pressure level data and hybrid coordinate data), AFWA's AGRMET land surface model output, ECMWF,

and other data a template; further details on the meaning of fields in a Vtable are provided in the section

on creating and editing Vtables. Ungrib can write intermediate data files in any one of three user-selectable formats: WPS – a new format containing additional information useful for the downstream programs; SI – the previous intermediate format of the WRF system; and MM5 format, which is included here so that ungrib can be used to provide GRIB2 input to the MM5 modeling system. Any of these formats may be used by WPS to initialize WRF, although the WPS format is recommended.

The **Metgrid** program horizontally interpolates the intermediate-format meteorological data that are extracted by the ungrib program onto the simulation domains defined by the geogrid program. The interpolated metgrid output can then be ingested by the WRF real program. The range of dates that will be interpolated by metgrid are defined in the "share" namelist record of the WPS namelist file, and date ranges must be specified individually in the namelist for each simulation domain. Since the work of the metgrid program, like that of the ungrib program, is time-dependent, metgrid is run every time a new simulation is initialized.

Control over how each meteorological field is interpolated is provided by the METGRID.TBL file. The METGRID.TBL file provides one section for each field, and within a section, it is possible to specify options such as the interpolation methods to be used for the field, the field that acts as the mask for masked interpolations, and the grid staggering (e.g., U, V in ARW; H, V in NMM) to which a field is interpolated. Output from metgrid is written in the WRF I/O API format, and thus, by selecting the NetCDF I/O format, metgrid can be made to write its output in NetCDF for easy visualization using external software packages, including the new version of RIP4.

5.2.2 WRF

The WRF model has two large classes of simulations that it is able to generate: those with an ideal initialization and those utilizing real data. The idealized simulations typically manufacture an initial condition file for the WRF model from an existing 1-D or 2-D sounding and assume a simplified analytic orography. The real-data cases usually require pre-processing from the WPS package, which provides each atmospheric and static field with fidelity appropriate to the chosen grid resolution for the model. The WRF model executable itself is not altered by choosing one initialization option over another (idealized vs. real), but the WRF model pre-processors (the real.exe and ideal.exe programs) are specifically built based upon a user's selection. Note that the WRF forecast model is identical for both of these initialization programs. In each of these initialization modules, the same sort of activities goes on:

1. Compute a base state / reference profile for geopotential and column pressure
2. Compute the perturbations from the base state for geopotential and column pressure
3. Initialize meteorological variables: u, v, potential temperature, vapor mixing ratio
4. Define a vertical coordinate
5. Interpolate data to the model’s vertical coordinate
6. Initialize static fields for the map projection and the physical surface; for many of the idealized cases, these are simplified initializations, such as map factors set to one, and topography elevation set to zero

5.3 SMOKE – Sparse Matrix Operation Kernel Emissions [5]

The MCNC Environmental Modeling Center (EMC) created the Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System to allow emissions data processing methods to integrate high-performance computing (HPC) sparse-matrix algorithms. The SMOKE system is a significant addition to the available resources for decision-making about emissions controls for both urban and regional applications. It provides a mechanism for preparing specialized inputs for air quality modeling research, and it makes air quality

forecasting possible. The SMOKE system continues to develop and improve at the University of North Carolina at Chapel Hill's Carolina Environmental Program (CEP).

SMOKE can process criteria gaseous pollutants such as carbon monoxide (CO), nitrogen oxides (NO_x), volatile organic compounds (VOC), ammonia (NH_3), sulfur dioxide (SO_2); particulate matter (PM) pollutants such as PM of 2.5 microns or less ($PM_{2.5}$) and PM less than 10 microns (PM_{10}); as well as a large array of toxic pollutants, such as mercury, cadmium, benzene, and formaldehyde. In fact, SMOKE has no limitation regarding the number or types of pollutants it can process. The purpose of SMOKE (or any emissions processor) is to convert the resolution of the emission inventory data to the resolution needed by an air quality model. Emission inventories are typically available with an annual-total emissions value for each emissions source, or perhaps with an average-day emissions value.

5.3.1 Emissions Inventories

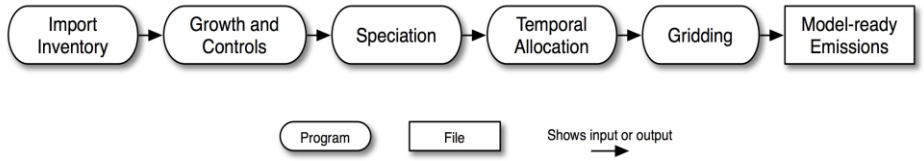
Emission inventories are divided into several source categories. These divisions stem from both differing methods for preparing the inventories and from different

characteristics and attributes of the categories (more on these terms later). Generally, emission inventories are divided into the following source categories: **Stationary area/Nonpoint sources** are treated as being spread over a spatial extent (usually a county or air district) and that are not moveable (as compared to nonroad mobile and onroad mobile sources). Because it is not possible to collect the emissions at each point of emission, they are estimated over larger regions. The EPA introduced the term "nonpoint" to replace "stationary area" in order to avoid confusion with the term "area source", which is used as a regulatory term in the toxics realm. However, "nonpoint" has not gained acceptance (thus far) by the criteria inventory/modeling community. Thus, in this manual we will use the term "stationary area" to refer to these sources when they are in criteria inventories, while we use the term "nonpoint" to refer to these sources when they are in toxics inventories. Examples of nonpoint or stationary area sources are residential heating and architectural coatings. Numerous sources, such as dry cleaning facilities, may be treated either as stationary area/nonpoint sources or as point sources; in particular, the toxics inventory contains numerous small sources (based on emissions) that are not inventoried as nonpoint sources because their locations are known and are provided. **Nonroad mobile sources** are Vehicular and otherwise movable sources that do not include vehicles that travel on roadways. These sources are also computed as being spread over a spatial extent (again, a county or air district). Examples of nonroad mobile sources include locomotives, lawn and garden equipment, construction vehicles, and boating emissions. These sources are included in both criteria and toxics inventories. **On-road mobile sources** are vehicular sources that travel on roadways. These sources can be computed either as being spread over a spatial extent or as being assigned to a line location (called a link). Data in on-road inventories can be either emissions or activity data. Activity data consists of vehicle miles traveled

(VMT) and, optionally, vehicle speed. Activity data are used when SMOKE will be computing emission factors via another model such as MOVES. Examples of on-road mobile sources include light-duty gasoline vehicles and heavy-duty diesel vehicles. On-road mobile sources are included in both criteria and toxics inventories. **Point sources** are identified by point locations, typically because they are regulated and their locations are available in regulatory reports. Point sources are often further subdivided into electric generating utilities (EGUs) and non-EGU sources, particularly in criteria inventories in which EGUs are a primary source of NO_x and SO_2. Examples of non-EGU point sources include chemical manufacturers and furniture refinishers. Point sources are included in both the criteria and toxics inventories. **Wildfire sources**, traditionally, have been treated as stationary area sources. More recently, data have also been developed for point locations, with day-specific emissions and hour specific plume rise (vertical distribution of emissions). In this case, the wildfire emissions are processed by SMOKE as point sources. **Biogenic land use data** characterize the type of vegetation that exists in either county total or grid cell values.

5.3.2 SMOKE's approach to emissions modeling

The paradigm for atmospheric emissions models prior to SMOKE was a network of pipes and filters. This means that at any given stage in the processing, an emissions file includes self-contained records describing each source and *all* of the attributes acquired from previous processing stages. Each processing stage acts as a filter that inputs a stream of these fully-defined records, combines it with data from one or more support files, and produces a new stream of these records. Redundant data are passed down the pipe at the cost of extra I/O, storage, data processing, and program complexity.



Using this method, all processing is performed one record at a time, without necessarily a structure or order to the records. The paradigm implemented in SMOKE came about from analyses indicating that emissions computations should be quite adaptable to high-performance computing if the paradigm were appropriately changed. For each SMOKE processing category (i.e., area, biogenic, mobile, and point sources), the following tasks are performed:

- Read emissions inventory data files.
- Optionally grow emissions from the base year to the (future or past) modeled year (except biogenic sources).
- Transform inventory species into chemical mechanism species defined by an AQM.
- Optionally apply emissions controls (except for biogenic sources).
- Model the temporal distribution of the emissions, including any meteorology effects.
- Model the spatial distribution of the emissions.
- Merge the various source categories of emissions to form input files for the AQM.
- At every step of the processing, perform quality assurance on the input data and the results.

SMOKE is designed to take advantage of these facts by formulating emissions modeling in terms of sparse matrix operations, which can be performed by optimized sparse matrix libraries. Specifically, the inventory emissions are

arranged as a vector of emissions sorted in a particular order, with associated vectors that include characteristics about the sources such as the state/county and SCCs. SMOKE then creates matrices that apply the control, gridding, and speciation factors to the vector of emissions. In many cases, these matrices are independent from one another, and can therefore be generated in parallel and applied to the inventory in a final "merge" step, which combines the inventory emissions vector (now an hourly inventory file) with the control, speciation, and gridding matrices to create model-ready emissions.

5.4 CAMx – Comprehensive Air quality Model with eXtensions

The Comprehensive Air quality Model with extensions (CAMx) is an Eulerian photochemical dispersion model that allows for integrated "one-atmosphere" assessments of air pollution (ozone, particulates, air toxics, and mercury) over spatial scales ranging from neighborhoods to continents. It is designed to unify all of the technical features required of "state-of-the-science" air quality models into a single open-source system that is computationally efficient, flexible, and publicly available. The model's Fortran source code is modular and well-documented. The Fortran binary input/output file formats are based on the Urban Airshed Model (UAM) convention and are compatible with many existing pre- and post-processing tools. Meteorological fields are supplied to CAMx from separate weather prediction models.

CAMx simulates the emission, dispersion, chemical reaction, and removal of pollutants in the troposphere by solving the pollutant continuity equation for each chemical species (l) on a system of nested three-dimensional grids. The Eulerian continuity equation describes the time dependency of the average species concentration (c_l) within each grid cell volume as a sum of all of the physical and

chemical processes operating on that volume. This equation is expressed mathematically in terrain-following height (z) coordinates as follows:

$$\frac{\partial c_l}{\partial t} = -\nabla_H \cdot V_H c_l + \left[\frac{\partial (c_l \eta)}{\partial z} - c_l \frac{\partial^2 h}{\partial z \, \partial t}\right] + \nabla \cdot \rho K \nabla (c_l / \rho)$$

$$+ \left.\frac{\partial c_l}{\partial t}\right|_{Emission} + \left.\frac{\partial c_l}{\partial t}\right|_{Chemistry} + \left.\frac{\partial c_l}{\partial t}\right|_{Removal} \qquad \textbf{Eq.(5.1)}$$

where V_H is the horizontal wind vector, η is the net vertical transport rate, h is the layer interface height, ρ is atmospheric density, and K is the turbulent exchange (or diffusion) coefficient. The first term on the right-hand side represents horizontal advection, the second term represents net resolved vertical transport across an arbitrary space- and time-varying height grid, and the third term represents sub-grid scale turbulent diffusion. Chemistry is treated by simultaneously solving a set of reaction equations defined from specific chemical mechanisms. Pollutant removal includes both dry surface uptake (deposition) and wet scavenging by precipitation.

CAMx perform simulations on three types of Cartesian map projections: Universal Transverse Mercator, Rotated Polar Stereographic, and Lambert Conic Conformal. CAMx also offers the option of operating on a curvi-linear geodetic latitude/longitude grid system. The vertical grid structure is defined externally, so layer interface heights may be specified as any arbitrary function of space and/or time. This flexibility in defining the horizontal and vertical grid structures allows CAMx to be configured to match the grid of any meteorological model that is used to provide environmental input fields.

5.5 The Gulf of Naples Geographic Model from WRF [6][7]

The goal in using WRF was to create some geographical domains centered on the Gulf of Naples in different time periods for comparison about temperature and pressure variations, winds directions in different seasons and from year to year.

The datasets used for with work were taken from **NCEP FNL** (Final) Operational Global Analysis data. These dates are on 1-degree by 1-degree grids prepared operationally every six hours. The analyses are available on the surface, at 26 mandatory (and other pressure) levels from 1000 millibars to 10 millibars, in the surface boundary layer and at some sigma layers, the tropopause and a few others. Parameters include surface pressure, sea level pressure, geopotential height, temperature, sea surface temperature, soil values, ice cover, relative humidity, u- and v- winds, vertical motion, vorticity and ozone.

WRF was focused on the definition of a geographical domain centered on Campania region., centered on the Gulf of Naples. Three Geographic domain were defined using WPS.:

- Parent Domain - **1020x1020 km** - Environmental Domain
- First Nest Domain - **450x450 km** - Boundary condition Domain
- Second Nest Domain - **120x120 km** - Model Domain

WPS is set to operate with a huge number of possible nests domains. The program needs **one parent domain** with general description of Lat/lon coord and central Point of the map, **a first nest** useful to create weathers boundary condition to the **model set on the second nest centred on the gulf of naples**

The three models are shown in Figures 5.3 and 5.4 5.5. In order to define a three-dimensional model with prognostic purposes as regards the movement of pollutants in the atmosphere has been necessary to pay attention on the topography of the model (Figure 5.6) and on the vertical levels in terms of variation of pressure and temperature.

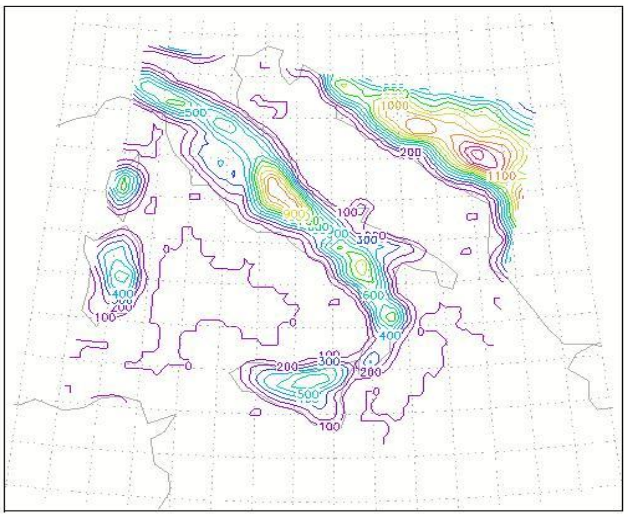


Fig.5.3: Parent Domain: 1020x1020km : Environmental Domain

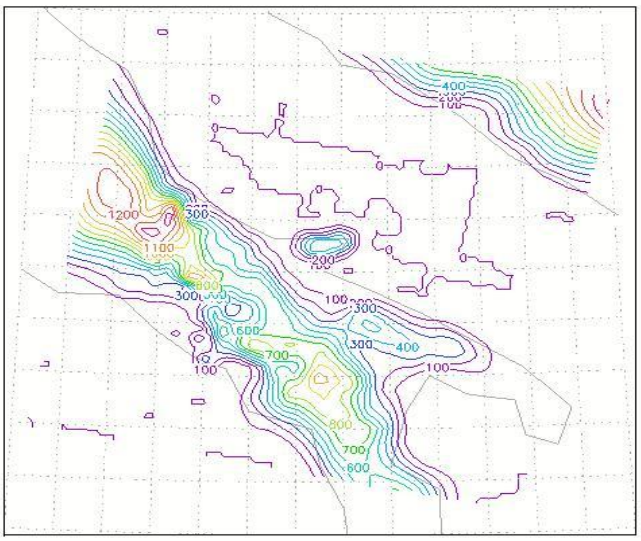


Fig.5.4: 1° Nest Domain: 450x450km : Boundary conditions Domain

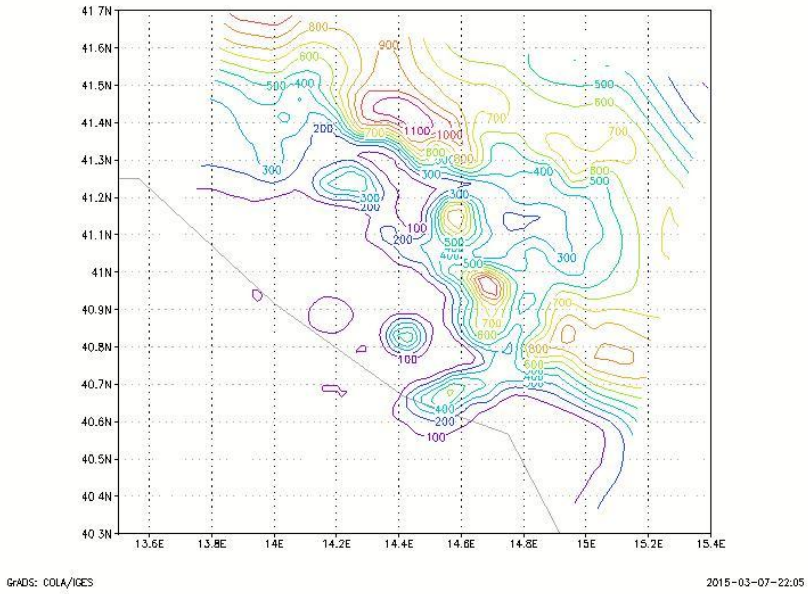


Fig.5.5: 2° Nest Domain: 120x120km : Model Domain set on gulf of naples

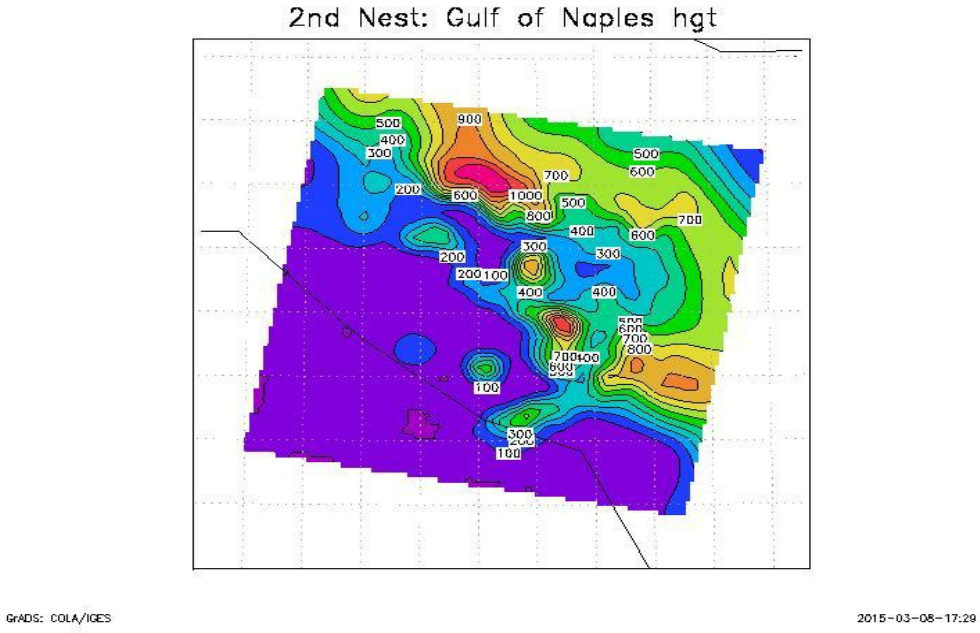


Fig.5.6: 2° Nest Domain: 120x120km : Contoured height levels with descriptions

Through about 15 km altitude in the troposphere are variations of temperature and pressure defined inside the thermal inversions of the atmosphere. With WRF has been possible to meet these variations of temperature and pressure within all 26 vertical levels which simulate tropospheric environment.

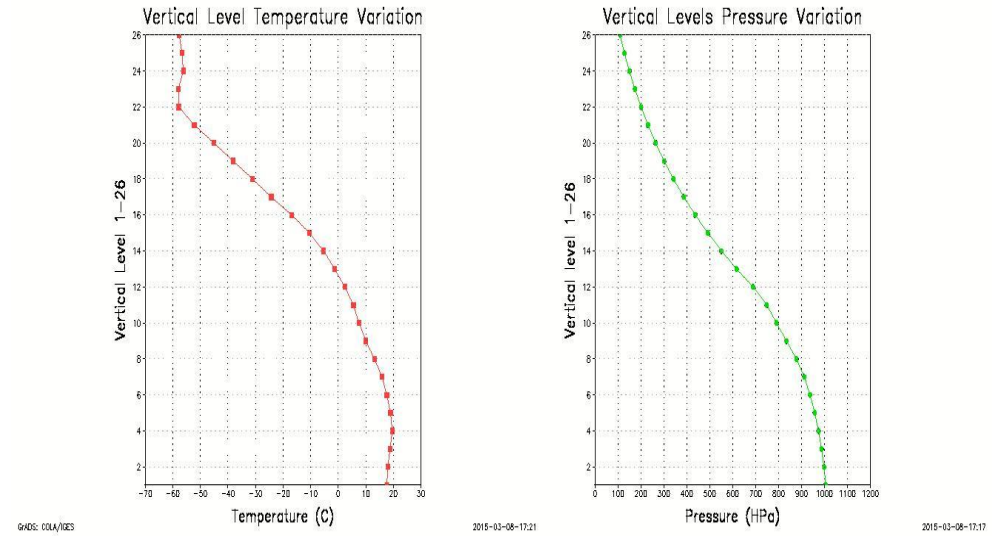


Fig.5.7: Temperature and Pressure variation across the 26 vertical levels of the domain. In red the temperature variation in °C, in green the pressure variation in HPa.

The same change of the temperature and the pressure was verified within a defined time domain in a 30 days. In Figure 5.7 is possible to observe how the trend of temperature change of the lower levels of the model is also followed by the trend of more high levels.

It was taken into consideration the model July 2013 to observe how the gradual increase of the temperature in the summer months is respected at all vertical levels proportionally. In Figure 5.8 you can see how the red curve on the first vertical level within the various tops and bottoms as daily and increases in average in the thirty days. The same trend with changes progressively less obvious is maintained even to the next levels.

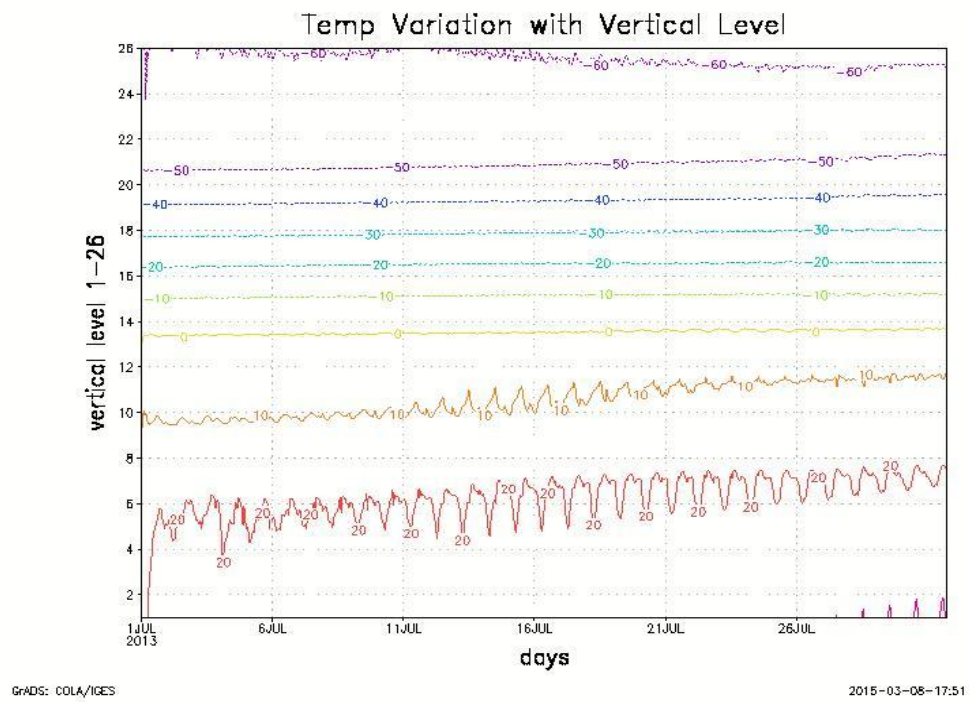
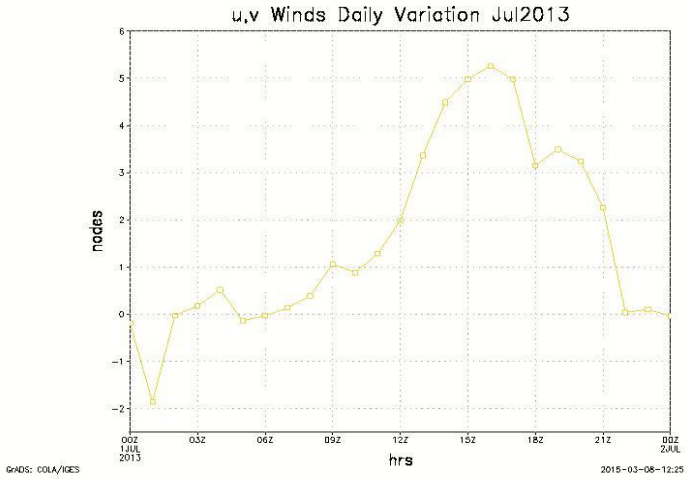


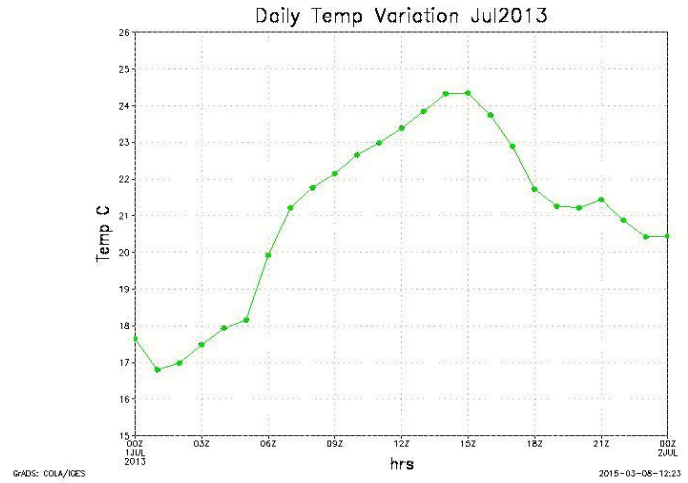
Fig.5.8: Temperature variation across the 26 vertical levels of the domain in a temporal period of 30 days July 2013 In red the temperature variation in °C, shows the min/max variation across the days

5.5.1 Monthly domains descriptions

The temporal domains chosen for the meteorological model are were in January and July 2012 to evaluate changes in temperature and pressure direction and intensity of the winds between the summer and the Fairy-tale winter months, and in July 2013 for purposes of comparison between seasonal trends similar after one year . In figures 5.9 - 5:11 a, b, c, respectively, you can see the daily change of the component u, v wind, temperature and atmospheric pressure for the months of January and July 2013 and July 2012.



(a)



(b)

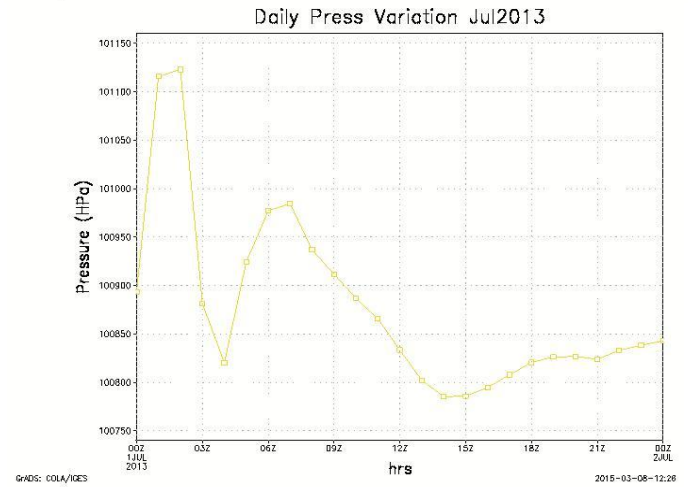


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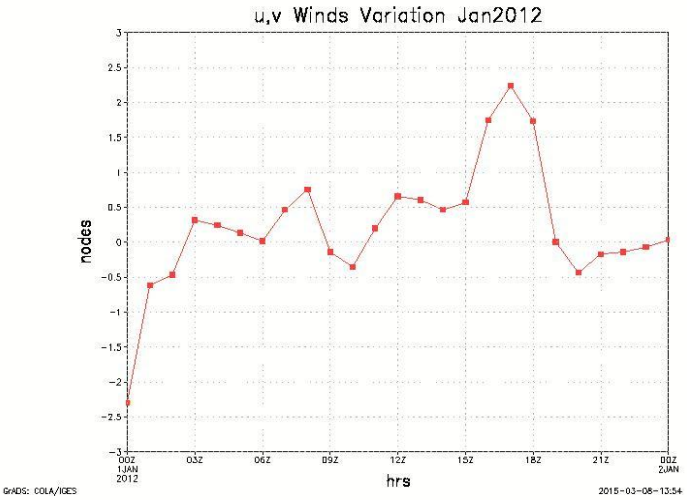
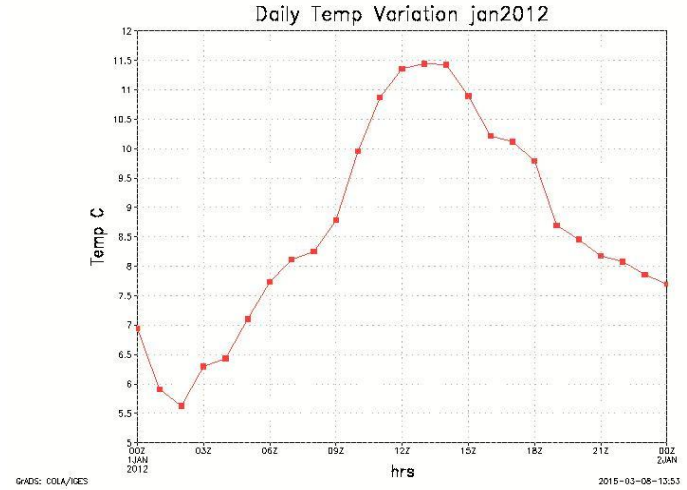
Fig.5.9: Daily variation of u,v winds direction (a)Temperature (b) Pressure (c) during July 2013



(a)



(b)

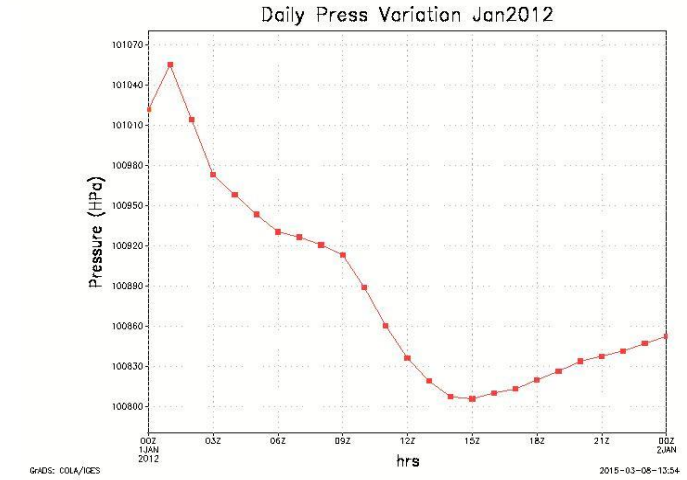


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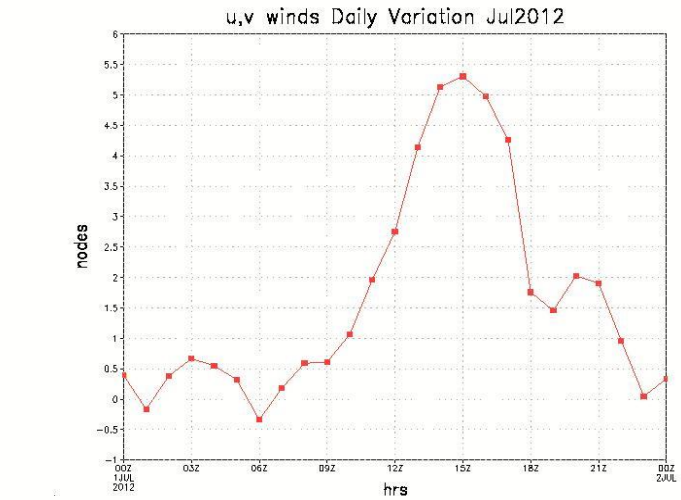
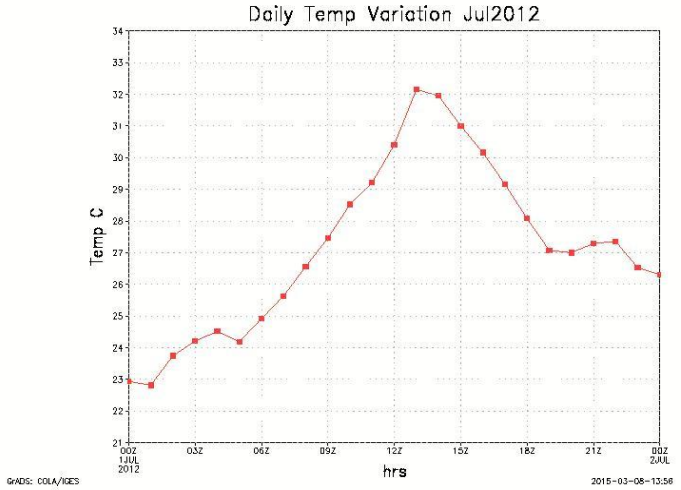
Fig.5.10: Daily variation of u,v winds direction (a)Temperature (b) Pressure (c) during January 2012



(a)



(b)

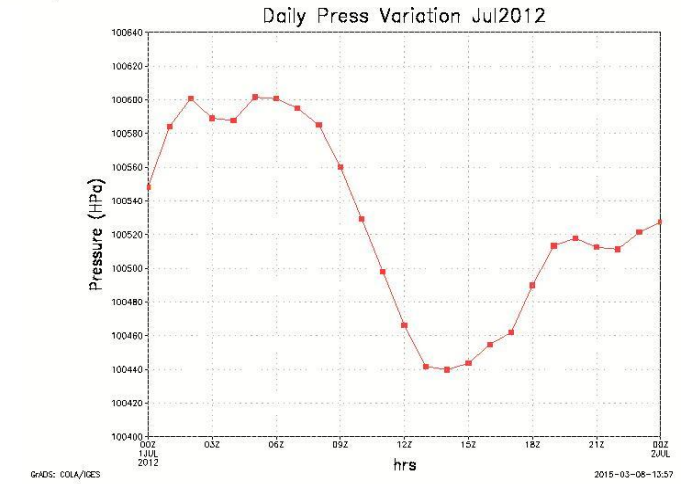


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Fig.5.11: Daily variation of u,v winds direction (a)Temperature (b) Pressure (c) during January 2012

The variations observed in the three models considered showed excellent agreement with the corresponding values measured experimentally by the reference to the air quality monitoring (ARPAC). The results obtained from the simulation of the three domains have given excellent results and represent the operational base for the future development of a system of on-line monitoring of air quality with respect to the main variable weather atmospheric chemistry.

5.6 SMOKE preparation for emissions models

Inventories used mainly come from database **ISPRA** (Higher Institute for the Protection and Environmental Research) and **EMEP** (the European Monitoring and Evaluation Program) and are related to the main air pollutants (NO_X, SO_2, NMVOCs, NH_3, PTS), sources emissive punctual regional and provincial, CO_2 emissions from transport vehicles, stationary emissions of greenhouse gases. The database concerning the Biogenic component a and land use is **MEGAN**, taken from the analysis program of air quality *CHIMERE*.

For the definition of a model for emissions of pollutants into the atmosphere is necessary to make a number of preliminary operations to set the program for the simulation. The choice and appropriate use of national and european inventories has great importance regarding atmospheric emissions. The use of inventories for emissions models Eulerian CTM (Chemical and Transport Models) requires the implementation of important preliminary steps. In fact, normally, an inventory is made of a single piece of data emission for each pollutant considered, from a given area territorial (province, municipalities ...) and to a specific time period (year). This type of information are far from those required by a Model CTM to which emissions must be provided to the hourly level on a regular grid of cells that constitutes the calculation domain. Moreover, in the transition from inventory to input modeling is necessary to make the chemical speciation of volatile organic

compounds and speciation of particulate particle size. Your use of the SMOKE model for the management of inventories available at national / European requires some preliminary preparation of adaptation of the system consisting of the definition of specific support files are able to consider the peculiarities of European data.

In particular in this work are defined the following files:

- **COSTCY** - definition of territorial bases (provinces, municipalities, EMEP cells ...)
- **SCCDESC** - classification of the emission sources
- **GRIDDESC** - definition of calculation grids of the projections of coordinates to be used

In addiction was performed the **integration of emission inventories** between **ISPRA** datasets and **EMEP** 50x50km gridded datasets.

5.6.1 COSTCY File

The file is used by SMOKE COSTCY to assign numeric codes to the various arias territorial dell'nventario considered in the management of emissions. Originally, for its application to the US data (the program is owned by the University of North Carolina) are defined in the file COSTCY codes "Country, State and County" by assigning a type code **CSSYYY:**

- **C** Country Code (1 digit: 0 to 99)
- **SS** State Code (2 digits: 0 to 99)
- **YYY** County Code (3 digits: 1 to 999)

Inventory management National / EU requires the consideration of inventories carried along territorial different.

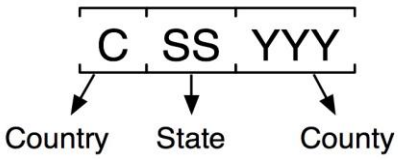

Fig 5.12: COSTCY file code description

For example, for application on a national scale was considered the use of the inventory ISPRA on a provincial and municipal use of the EMEP inventory based on a 50x50 km grid. According to this logic, it was decided to reserve the code "Country" to the type of inventory and to define case codes "State" and "County" to disaggregate the data inventory seconds ISTAT codes with the following assignment CSSYYY:

- C Country code 0 and 1 for Italy
- SS ISTAT code of the Province
- YYY ISTAT code of the City

In this way the code CSSYYY coincides with the ISTAT code for municipalities within the provinces from 1 to 99 while the provinces with ISTAT code greater than or equal to 100 country code takes the value of 1 while you are queues that is not allowed the value 00 is defined in the following way:

$$SS = (ISTAT_{prov} + 1) - 100$$

where $ISTAT_{prov}$ is the ISTAT province code.

5.6.2 SCCDESC File

The file contains SCCDESC classification of sources with respect to which it is defined the emissions inventory. Originally this file contains the classification SCC (Source Code Classification) used in the United States than the SNAP defined in the European context is more detailed as to the different types of sources also considers the fuel used and the presence of systems to reduce emissions .

The SCC code (8 or 10 digits) is defined through a hierarchical structure of the type:

- code SCC 8 fields: A BB CCC DD
- code SCC 10 fields: AA BB CCC DDD

where A / AA corresponds to level 1 (the most generic and identifiable with macrosectors nomenclature SNAP), BB to level 2 to level 3 CCC, DD / DDD to Level 4, to further detail. The adaptation of this classification to the European data was done by defining a schema for the SCC code like:

MMSSCCxxxx

where the correspondence with the SNAP nomenclature is the following:

- MM - macrosector
- SS – industry
- CC - category
- xxxx - available fields to consider a further subdivision of technology, the type of fuel or the abatement system

The hierarchical structure of the code is important as it facilitates the definition of cross-reference tables used to assign each category emissive their respective indication of the breakdown (spatial, temporal, speciation).

5.6.3 GRIDDESC File

The file GRIDDESC contains information related to the systems of coordinates and to the grids of the calculation. The file can contain information about different coordinate systems and more computing grids. This file has been added to the coordinate system POLAR_CAMX_IT based on stereographic polar coordinates with pole at the point of LAT / LON of 41 ° N and 14.2 ° E.

In this coordinate system is then defined a grid coincides with that will be used by CAMx.

5.6.4 Integration of emission inventories

The integration of emission inventories in the model SMOKE covered the following databases:

- Provincial ISPRA 2010 disaggregated at the municipal level
- Emissions EMEP for the year 2010 with emissions of EMEP grid 50x50 km^2 for the foreign part included in the calculation domain modeling

The original EMEP grid (Figure 5.12) is defined in a particular polar stereographic projection having the axes oriented in the north-south direction, this characteristic makes it difficult to manage with conventional mapping software. To facilitate the use of data expressed in the EMEP grid the European Agency for the Environment has taken charge of transforming the EMEP grid projection standards adopted by the Agency: Projection Lambert azimuthal equal-area represented in Figure 5.13.

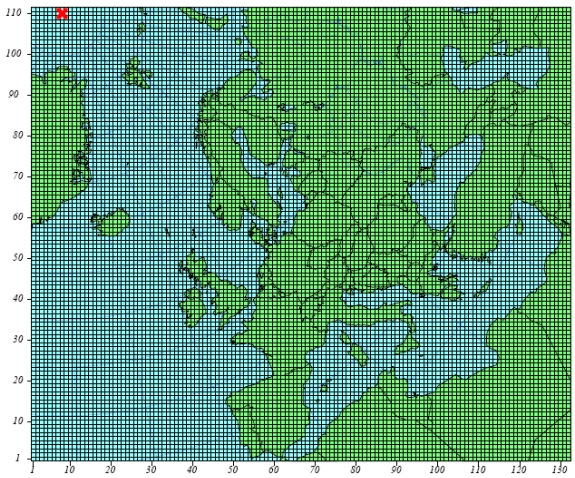

Fig.5.12 Emissive domain for EMEP Domain

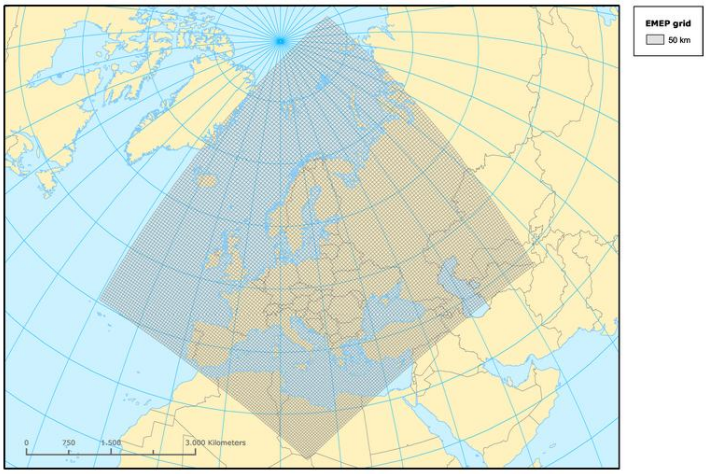

Fig.5.1 ıual-area (EEA: http://dataservice.eea.europa.eu)

For each cell EMEP (Figure 5.14) has been assigned the province (or municipality) prevailing defined as that of greater extension within each cell determined based on the official "country fraction grid" available on the EMEP website.

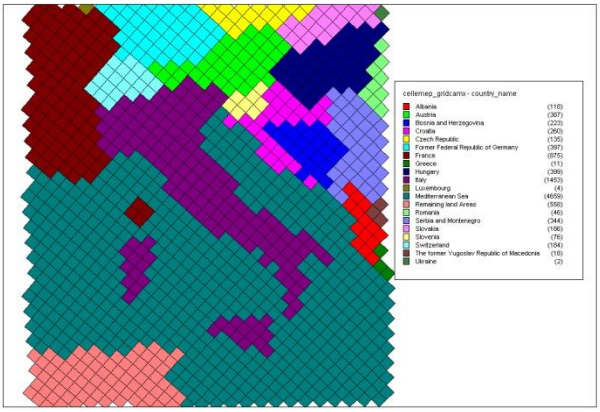

Fig.5.14 Association between state and region prevalent for each cell EMEP falling in the domain of modeling system

For the purpose of modeling it was decided to use the preprocessor emissive SMOKE that required rewriting data in the format IDA. To this end the program has been implemented IDAconvert.f90 which produces a file of emissions areal arinv.emep2010.ida.txt (Table 5.1).

Posizione	Nome	Descrizione
1 - 2	STID	Cod. Provincia
3 - 5	CYID	Cod. Comune
6 - 15	PLANTID	Macro*10000'___000'
17 - 25	ANN1	CO (short tons/yr)
64 - 72	ANN2	NH_3 (short tons/yr)
111 - 119	ANN3	NO_X (short tons/yr)
158 - 166	ANN4	PM10 (short tons/yr)
205 - 213	ANN5	PM2.5 (short tons/yr)
252 - 260	ANN6	SO_2 (short tons/yr)
299 - 307	ANN7	COV (short tons/yr)

Tab 5.1: File formatting arinv.emep2010.ida.txt

5.7 Conclusions

In this PhD work was addressed for the first time in the Department of Chemical Sciences of the University of Naples Federico II the difficult subject of the analysis of air quality. The project in collaboration with the Laboratory *Ambiente & Salute* - LAS - allowed us to study sampling techniques commonly used in environmental monitoring during a campaign of air monitoring in the former industrial area east of Naples - San Giovanni in Teduccio. Also, were optimized standard procedures for the determination of heavy metals and polycyclic aromatic hydrocarbons in particulate matter gravimetric filters , and has been

developed a new method for the parallel determination of the inorganic component of the atmospheric particulate PM_{10}.

The project in collaboration with the City of Naples has provided the implementation of a simulation weather and atmospheric emissions models act to the next realization of a prognostic model of air quality monitoring useful to citizenship of the metropolitan area of Naples.

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